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Citation for published version (APA):

Beekenkamp, P. (1965). *Colour centres in borate, phosphate and borophosphate glasses*. [Phd Thesis 1 (Research TU/e / Graduation TU/e), Chemical Engineering and Chemistry]. Technische Hogeschool Eindhoven. https://doi.org/10.6100/IR25966

DOI:

[10.6100/IR25966](https://doi.org/10.6100/IR25966)

Document status and date:
Published: 01/01/1965

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

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COLOUR CENTRES IN BORATE, PHOSPHATE AND BOROPHOSPHATE GLASSES

P. BEEKENKAMP

COLOUR CENTRES IN BORATE, PHOSPHATE AND BOROPHOSPHATE GLASSES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
IN DE TECHNISCHE WETENSCHAPPEN AAN DE
TECHNISCHE HOGESCHOOL TE EINDHOVEN
OP GEZAG VAN DE RECTOR MAGNIFICUS
PROF. DR. K. POSTHUMUS, HOOGLERAAR IN DE
AFDELING DER SCHEIKUNDIGE TECHNOLOGIE,
VOOR EEN COMMISSIE UIT DE SENAAT TE
VERDEDIGEN OP DINSDAG 21 DECEMBER 1965
DES NAMIDDAGS TE 4 UUR

DOOR

PIETER BEEKENKAMP

GEBOREN TE HOEK VAN HOLLAND

DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE PROMOTOR
PROF. DR. J. M. STEVELS.

Aan mijn vrouw
Aan Suzan en Heleen

CONTENTS

1. COLOUR CENTRES IN GLASSES

1.1. Introduction

The studies published nowadays on colour centres in glasses tend more and more in the direction of a fundamental investigation of the structure rather than a phenomenological description of these colour centres in various glasses. This trend has been accelerated by the rapid development of more sensitive electron-spin-resonance (ESR) equipments in recent years. The combined information obtained from ESR- and optical-absorption spectra has led to a better understanding of the structure of the glasses and of the radiation-induced imperfections, which are referred to as colour centres. In this study an attempt will be made to derive from optical and ESR investigations improved models for the structure of the borate, phosphate and borophosphate glasses and the colour centres induced in them by X-rays.

1.2. Radiation effects in glass

Various types of radiation interact with glass, causing a certain discolouration. This discolouration has been studied by many authors in various glasses and has been explained in terms of certain imperfections. In accordance with the nomenclature used for imperfections which give rise to the colouration of alkali-halide crystals, these imperfections in glass are also called colour centres. The different types of radiation, such as u.v. light, X- and gamma-rays, all give rise to the same types of colour centres in a certain glass, only differing in the intensities of the colouration produced (see e.g. ref. 1). The various kinds of radiation are absorbed in solids in different ways, depending on their energy. Ultraviolet light as well as X-rays are mainly absorbed by the photo effect. Gamma-rays may also be absorbed by means of the Compton effect and pair formation. All three effects produce free electrons with an energy which is a function of the incident-photon energy. These free electrons may in their turn produce changes in the structural units of the glass involved.

For silicon-oxygen networks the possible structural units have been systematized by Stevels and Kats [2]. One of the types of structural units believed to be present in a sodium-silicate glass, for example, contains a non-bridging oxygen ion, its excess of negative charge being compensated by an interstitial sodium ion. Upon irradiation an electron of the non-bridging oxygen ion may be removed, whereafter the sodium ion — no longer required as charge compensator — may move to another site in the network now acting as an electron trap. This reaction is represented by the equation

$$\text{D-unit *)} \quad\rightleftharpoons\quad \text{Q-centre *)} \quad + Na^+ + e. \qquad (1.1)$$
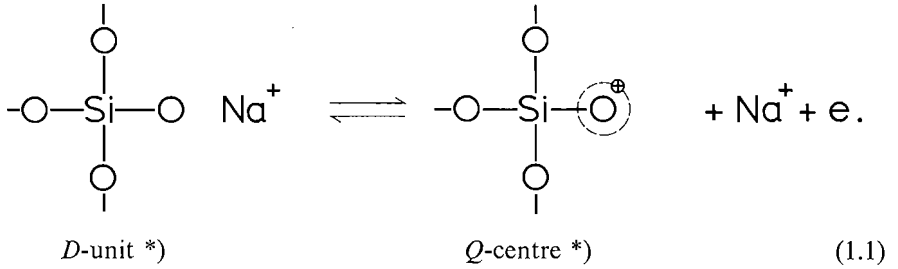
In a glass of composition $0.30\ Na_2O\ .\ 0.70\ SiO_2$ the number of D-units — if the excess oxygen ions introduced by the sodium oxide is only taken up in this way — is of the order of magnitude of $10^{22}/cm^3$. However, Van Wieringen and Kats [3] showed by means of ESR measurements that the number of Q-centres induced by irradiation is of the order of magnitude of 10^{18} - $10^{19}/cm^3$, which proves that only a small part of the D-units could be converted into stable Q-centres. The presence of D-units is necessary but not sufficient for the formation of stable Q-centres. Apparently an additional stabilizing factor is involved, which may depend on the constitution of the direct environment of the centre or in some cases on the presence of an impurity nearby the centre. In their study on irradiated crystalline quartz Stevels and Volger [4] introduced the concept of "mooring" for sites in the lattice where the sodium ions freed by reaction (1.1) find a stable position, which they believed to consist of an already existing irregularity, imperfection or impurity (foreign ion) in the lattice. These sodium ions may capture an electron, forming a colour centre. In this study the concept "mooring" may be used for all the colour centres to be discussed if one modifies the definition as follows: a mooring consists of a certain structure of the network or an impurity in the direct environment of the centre formed upon irradiation, which stabilizes this centre.

Summarizing, the effects of the irradiation can be described in the following way. Various structural units (intrinsic or containing impurities) can be distinguished in a glass. Certain types of units can be converted into colour centres and will therefore be referred to as *active structural units*. However, in practice active structural units will only be converted into *stable colour centres* (under the chosen experimental conditions) if stabilizing *moorings* are present. These active structural units will hereafter be referred to as *progenitors*.

These considerations lead to a theory of the formation of colour centres described in the following section.

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*) This nomenclature has been proposed by Stevels and Kats [2].

1.3. A theory of the formation of colour centres

1.3.1. *The maximum number of colour centres formed upon irradiation*

In a vitreous system a number N_A of a given type of structural units may be present which are active structural units. However, only a part p of these active structural units (the progenitors) will be converted into stable colour centres, this fraction being determined by two factors:

(1) An active structural unit may be too stable at the temperature involved to be converted into a colour centre by a certain type of radiation.

(2) The stabilizing action of a mooring will be a function of the temperature. Therefore it may be expected that certain active structural units become progenitors by a change of the temperature.

Now $(1 - p)N_A$ active structural units remain unchanged. However, during irradiation the moorings of a number of active structural units may be changed so that an additional number of progenitors is formed. If this mechanism is operative for a fraction q, the total maximum number of stable colour centres to be formed upon irradiation or the total number of progenitors will be $pN_A + q(1 - p) N_A$. The fractions p and q are determined by the glass composition, the energy of the radiation used and the temperature.

1.3.2. *The kinetics of the formation*

The number of progenitors present before irradiation is (cf. sec. 1.3.1)

$$N_{P_0} = pN_A. \tag{1.2}$$

As the absorption of radiation is a statistical process, the number of progenitors will decrease according to

$$N_P = N_{P_0} \exp(-\lambda_P r), \tag{1.3}$$

where r = radiation dose,

  λ_P = rate constant

and N_P = number of progenitors after dose r.

The number of colour centres as a function of the dose r follows from eq. (1.4) (fig. 1.1):

$$N_C = N_{P_0}\{1 - \exp(-\lambda_P r)\}. \tag{1.4}$$

During irradiation additional progenitors are formed from a number of active structural units N_{R_0}, which will be called potential progenitors (cf. sec. 1.3.1):

$$N_{R_0} = q(1 - p)N_A. \tag{1.5}$$

The number of potential progenitors will thus decrease according to

$$N_R = N_{R_0} \exp(-\lambda_R r) \tag{1.6}$$
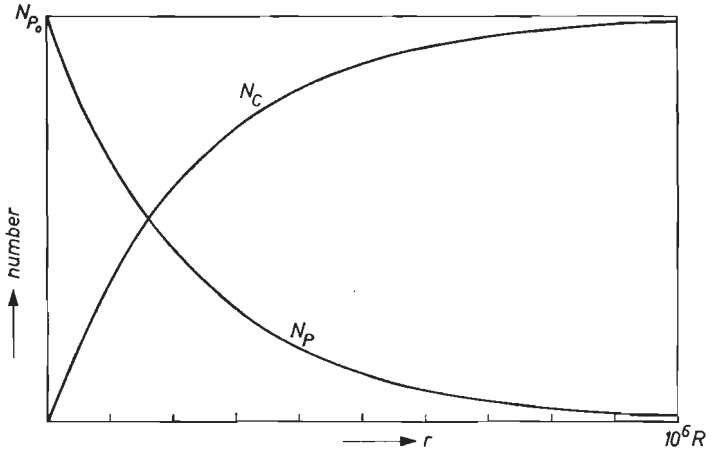
Fig. 1.1. The numbers of progenitors (N_P) and colour centres (N_C) as a function of the radiation dose r (cf. eqs (1.3) and (1.4)).

and will form an additional number of progenitors N_P', which subsequently will be converted into a number of colour centres N_C'. During irradiation the number of additional progenitors N_P' will decrease at the same rate as the initial progenitors N_P. Hence

$$dN_P' = (\lambda_R N_R - \lambda_P N_P')dr = \{\lambda_R N_{R_0} \exp(-\lambda_R r) - \lambda_P N_P'\}dr. \tag{1.7}$$

As $N_P' = 0$ for $r = 0$ it follows from eq. (1.7) after integration:

$$N_P' = [\lambda_R N_{R_0}/(\lambda_P - \lambda_R)] \{\exp(-\lambda_R r) - \exp(-\lambda_P r)\}. \tag{1.8}$$

Since $N_{R_0} = N_R + N_P' + N_C'$ for each value of r, it follows that (fig. 1.2)

$$N_C' = N_{R_0}\{1 - [1 + \lambda_R/(\lambda_P - \lambda_R)] \exp(-\lambda_R r) - [\lambda_R/(\lambda_R - \lambda_P)] \exp(-\lambda_P r)\}. \tag{1.9}$$
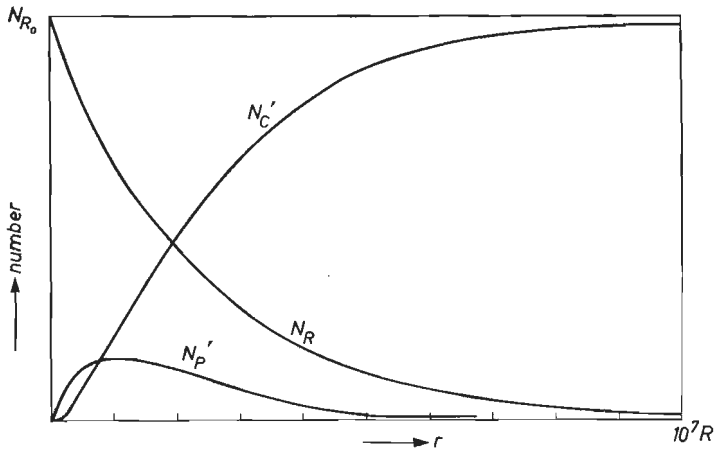
Fig. 1.2. The numbers of potential progenitors (N_R), progenitors (N_P') and colour centres (N_C') as a function of the radiation dose. Here λ_P has been chosen to be equal to $10 \lambda_R$.

The total number of colour centres which may be formed upon irradiation is

$$N_{C_{tot}} = N_C + N_{C'}. \tag{1.10}$$

Combination of eqs (1.4), (1.9) and (1.10) gives $N_{C_{tot}}$ as a general solution. Equation (1.9) may be simplified with the aid of certain approximations. If $\lambda_P \gg \lambda_R$ (in words: if the rate of formation of stable colour centres is much larger than the rate of formation of the additional progenitors), then

$$N_{C'} = N_{R_0} \{1 - \exp(-\lambda_R r)\}. \tag{1.11}$$

If $\lambda_R r \ll 1$,

then
$$N_{C'} = \lambda_R N_{R_0} r. \tag{1.12}$$

It may be seen from the above that the number of colour centres is *not* a simple function of r (= radiation dose). Therefore, generally speaking, a quantitative comparison of the numbers of colour centres induced by the same dose r in different glasses as a function of their composition will be of doubtful value. However, if

$$f_a N_a(r) = f_b N_b(r) = f_c N_c(r), \tag{1.13}$$

where $N_i(r)$ is the number of colour centres in a glass of composition i after a radiation dose r and f_i is a constant for the glass of composition i, it is possible to compare these numbers in a quantitative way. A slight deviation from this condition still allows a semi-quantitative comparison, which will do in the cases where certain trends in the formation of coulour centres are considered in series of glasses with a gradually changing composition. It must be noted here that the bleaching effects occurring directly after irradiation have not been taken into account. However, if all experimental data on the number of colour centres are recorded after such a period that the equilibrium number of colour centres has been practically achieved — at the temperature and the radiation dose in question — the relations concerning the numbers of colour centres given in this section may be used.

It must be emphasized that in certain cases colour centres of one type may be converted into centres of another type after prolonged irradiation. In such cases the number of colour centres of the first type can be calculated by a procedure similar to that given above, with the additional condition that the colour centres of the first type are the progenitors of the second type.

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2. EXPERIMENTAL METHODS

2.1. Preparation of the samples

All the glasses investigated were prepared from reagent-grade chemicals. After the batch constituents had been mixed thoroughly, they were melted in an electric furnace with overhead heating by silicon-carbide rods. The firing was continued at the required temperature until frothing and bubbling ceased. The borate and borophosphate glasses were melted in platinum crucibles, the phosphate glasses in zirconia crucibles. Generally, the samples for optical measurements were ground and polished with carborundum and diamond powder, respectively, in kerosene. However, in some cases the glass obtained was too hygroscopic to be treated in this way. Especially the phosphate glasses with a low content of metal oxide have to be handled in a dry atmosphere. Two methods have been developed to overcome the difficulties in preparing optical samples of hygroscopical glasses:

(a) The melt is pressed out between two polished steel slabs (13% chromium), which are heated at such a temperature that the surface of the glass sample becomes sufficiently smooth. The sample is allowed to cool slowly between the steel slabs in a dry box, which is provided with a stream of 50 l/min dry air. Inside this box, the glass sample is mounted in a Dewar vessel (fig. 2.1) for optical measurements, which then is evacuated. The windows of this Dewar vessel are made of high-quality fused silica, which remains uncoloured upon irradiation in the measuring range ("Spectrosil" quality, from "The Thermal Syndicate Ltd.").

(b) The glass sample is ground and polished rapidly with carborundum and *water*. The wet, sticky surface of the sample is covered by two thin plates of fused silica, which remain practically unchanged by radiation doses sufficient to colour the glass sample. The two plates are fixed to each other by a quick-drying adhesive *). This method is only applicable to glasses with a transparent, sticky hydrolysis product.

The samples for electron-spin-resonance (ESR) measurements (dimensions: $15 \times 9 \times 2$ mm^3) were directly formed from the melt in a graphite mold. The hygroscopic samples are kept out of contact with the air as much as possible.

2.2. Introduction and detection of the colour centres

The colour centres were introduced in the glasses by irradiation with X-rays (equipment used: Müller MH 151/S, 150 kV, 15 mA, with a maximum dose rate at the tube of $1 \cdot 2.10^6$ R/h).

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*) This method has been developed by Mr H. J. A. van Dijk; the fused-silica plates were kindly provided by Dr A. Kats.
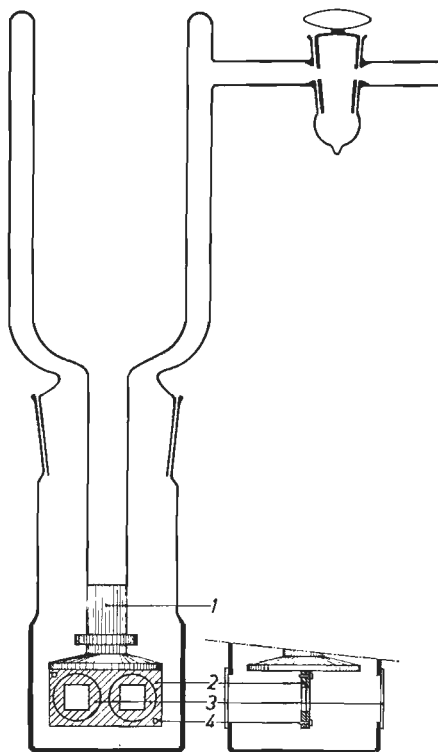
Fig. 2.1. Dewar vessel for optical-absorption measurements at low temperatures: (1) glass-to-metal seal, (2) brass sample holder, (3) "Spectrosil" windows, (4) screws.

For the optical measurements at room temperature, the non-hygroscopic samples were irradiated in air, and the hygroscopic ones in an evacuated vessel (for the sake of convenience, the Dewar vessel of fig. 2.1 was used).

For the low-temperature optical measurements, all irradiations were performed in the Dewar vessel of fig. 2.1 (in which the measurements were also made).

For the ESR measurements at room temperature, the non-hygroscopic samples were irradiated in air. The hygroscopic samples were irradiated in an evacuated vessel. It was not possible to carry out the ESR measurements in this same vessel, so these samples were then provided with a quick-drying coating as a protection against the air during measurement.

For the low-temperature ESR measurements all samples were irradiated in a polyethylene-foam vessel filled with liquid nitrogen, and then transferred to a small Dewar vessel fitted to the waveguide (fig. 2.2) for the measurements.

The *optical spectra* in the range of 1850-12000 Å were recorded by a Beckman DK2 spectrophotometer. The optical path of the equipment was provided with dry nitrogen in order to obtain better measuring conditions in the "far" u.v.
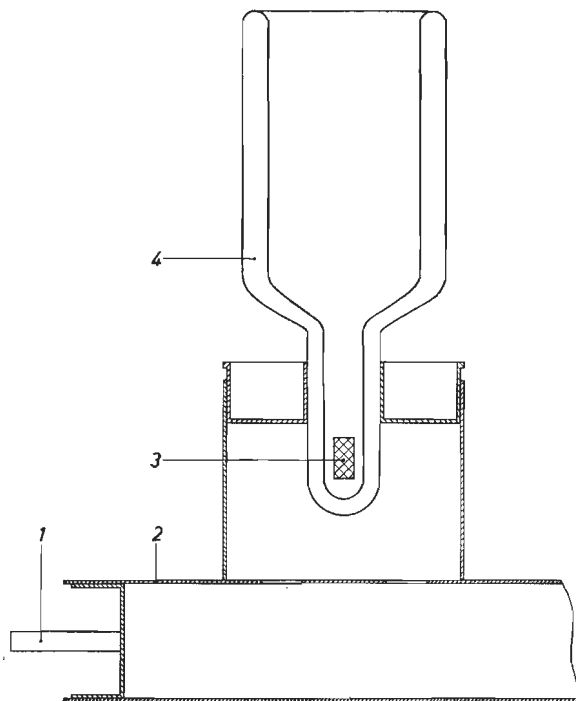
Fig. 2.2. Dewar vessel for ESR measurements at low temperatures, mounted in a wave guide: (1) piston, (2) wave guide, (3) sample, (4) fused-silica dewar vessel.

range (1850-2000 Å). However, the colour-centre spectra obtained in this region are less reliable, owing to the following factors:

— the transmission of the fused-silica prism is more wavelength-dependent in this range;
— the unirradiated samples of the glasses under investigation show a strong intrinsic absorption in this range;
— the poor optical quality of the samples often gives rise to a stronger absorption by scattering and reflexion at shorter wavelengths.

Therefore conclusions from the optical measurements in this "far" u.v. range must be rather tentative. Apart from the factors effecting the precision of the optical spectra in the " far" u.v., a *quantitative* comparison of the spectra of the whole range is still somewhat doubtful. In general the precision of the optical spectra is adversely effected by the following differences between the various glasses:

— the difference in hygroscopical effects on the surface of the samples, which could not be completely avoided;
— the difference in optical quality of the samples, due to inhomogeneities in the bulk and the difference in polishing properties.

The *electron-spin-resonance* (ESR) measurements were performed with a Varian 9500 Mc/s instrument. The same resonance cavity (type TE 011) was used for room-temperature and for liquid-nitrogen measurements. A fused-silica sample holder was used for the room-temperature measurements, and the small Dewar vessel of fig. 2.2 for the low-temperature measurements. The precision of the ESR spectra is effected by:

— the difference in dielectric losses of the various samples;

— a shift in the sensitivity of the ESR equipment over a longer period of time. These effects only allow a *semi*-quantitative comparison of the experimental results for different samples. Results obtained from the same sample after different treatments may be discussed in a quantitative way. Besides the restrictions mentioned above, all the limitations to a quantitative discussion of the experimental results given in sec. (1.3.2) are still valid.

Another effect which obscures the optical and ESR spectra is the overlapping of neighbouring absorption bands. Computer methods have been used by several authors [1,2] to overcome this difficulty, assuming that the induced absorption bands may be taken to be Gaussian. This method is significant only with highly accurate spectra.

2.3. Some theoretical remarks on the electron-spin-resonance (ESR) spectra

2.3.1. *Introduction*

Electron-spin resonance (also: electron paramagnetic resonance) is based on the direct transitions between Zeeman components of a particular electronic state, usually the lowest one. The transitions are induced by a coupling of the magnetic dipole moment of the resonating electrons to the magnetic component of the incident microwave radiation [3,4]. The classical resonance condition for a free electron in a magnetic field H_0 is given by

$$h\nu = g\beta H_0 = 2\cdot0023\beta H_0, \tag{2.1}$$

where h is Planck's constant, ν is the frequency of the microwave radiation applied perpendicular to H_0, β is the Bohr magneton ($= eh/4\pi mc$), and g is the spectroscopic splitting factor, being $2\cdot0023$ for a free electron. If the resonating electrons are not free, as is the case in colour centres, the resonance condition is somewhat modified. Neighbouring centres and nuclei may contribute to the local magnetic field, if they have a magnetic moment. Furthermore, the electrical field of the glass network gives rise to a change in the local magnetic field (spin-orbit coupling). These effects are incorporated in an effective g-factor, which is the determining factor for a particular unpaired electron in, for instance, a colour centre:

$$h\nu = g_{\text{eff}}\ \beta\ H_0. \tag{2.2}$$

For the analysis of the electron-spin resonance a generalized procedure has been given by Abragam and Pryce [5] for the resonance of transition elements in crystals. The characteristic energies E are determined by a proper spin-Hamiltonian operator H applied to the effective spin wave function ψ [6]:

$$H\psi = E\psi. \tag{2.3}$$

An appropriate spin Hamiltonian, which takes into account an axially symmetrical crystal field and the hyperfine splitting caused by an adjacent nucleus (both of which effects occur in the ESR spectra of irradiated glasses) is

$$H = \beta\{g_{||}H_zS_z + g_\perp(H_xS_x + H_yS_y)\} + AS_zI_z + B(S_xI_x + S_yI_y), \tag{2.4}$$

where the principal axes x, y and z are the same in all terms, and

β = Bohr's magneton = $eh/4\ \pi m_{electron}c$,
$g_{||}$ = effective g-factor parallel to the axis of symmetry,
$g_\perp$ = effective g-factor perpendicular to the axis of symmetry,
S = effective electron spin,
I = nuclear spin,
H = magnetic-field strength,
A = hyperfine-splitting tensor parallel to the axis of symmetry,
B = hyperfine-splitting tensor perpendicular to the axis of symmetry.

The first term of eq. (2.4) represents the splitting of the $(2S + 1)$ spin multiplets by the applied field. In colour centres an unpaired electron always has a spin $S = \frac{1}{2}$, hence $(2S + 1) = 2$, which gives two energy levels and thus one transition possibility. The second and the third terms represent the hyperfine-splitting interaction caused by a nucleus adjacent to the unpaired electron.

2.3.2. The spectra of glasses

Hyperfine splitting is observed in the ESR spectra of the glasses described in this thesis. A derivation will therefore be given here of the line shapes which may be expected in a glass spectrum with hyperfine splitting.

Bleany [7] showed that the ESR energy $h\nu_0$ corresponding to the Hamiltonian of eq. (2.4) in the case of a single crystal can be written as

$$h\nu_0 = g\beta H + M_I(A^2g_{||}{}^2\cos^2\theta + B^2g_\perp{}^2\sin^2\theta)^{1/2}\ g^{-1}, \tag{2.5}$$

where

$$g^2 = g_{||}{}^2\cos^2\theta + g_\perp{}^2\sin^2\theta, \tag{2.6}$$

M_I is the magnetic quantum number of a nucleus with spin I and θ is the angle between the symmetry axis and the direction of the applied magnetic field.

For paramagnetic centres in a glass, which have an equal probability for all orientations, the number of centres (dN) whose symmetry axis make an angle to the applied magnetic field of between θ and $\theta + d\theta$, is given by

$$dN = \tfrac{1}{2}N_0 \sin\theta\, d\theta, \tag{2.7}$$

where N_0 is the total number of centres [8]).

The transition probability is approximately independent of the orientation and the absorption intensity arising from the molecules lying between θ and $\theta + d\theta$ is, therefore, proportional to the number dN lying between these angles. The intensity of absorption in a range of magnetic field between H and $H + dH$ is proportional to $|dN/dH|$:

$$|dN/dH| = (dN/d\theta)|d\theta/dH|; \tag{2.8}$$

$dN/d\theta$ follows from eq. (2.7); $d\theta/dH$ can be derived from eq. (2.9), which is a modification of eq. (2.5):

$$H = (1/g\beta)(h\nu_0 - KM_I/g), \tag{2.9}$$

where

$$K^2 = g_{||}^2 A^2 \cos^2\theta + g_\perp^2 B^2 \sin^2\theta \tag{2.10}$$

and g^2 is given by eq. (2.6). The expression for dN/dH is [9])

$$dN/dH = \tfrac{1}{2}N_0 \left[[(2\cos\theta)/g^2]\, [(g_{||}^2 - g_\perp^2)\, h\nu_0/2g\beta + \right.$$
$$\left. + (M_I/\beta)\, \{(g_{||}^2 A^2 - g_\perp^2 B^2)/2K - K(g_{||}^2 - g_\perp^2)/g^2\}] \right]^{-1}. \tag{2.11}$$

If the paramagnetic centre experiences a spherically symmetric crystalline field, characterized by

$$g = g_{||} = g_\perp \text{ and } A = B, \tag{2.12}$$

it follows from eqs (2.5) and (2.6) that the hyperfine spectrum consists of $2I + 1$ equally spaced hyperfine lines.

In the case where eq. (2.11) holds generally (axially symmetric crystalline field) one finds two sets of $2I + 1$ peaks. The locations of these peaks are given by

$$H_{||}(M_I) = (h\nu_0 - M_I|A|)/g_{||}\beta \tag{2.13}$$

and

$$H_\perp(M_I) = (h\nu_0 - M_I|B|)/g_\perp\beta. \tag{2.14}$$

If it is assumed that $g_{||} > g_\perp$, $I = 3/2$ (cf. sec. 3.3) and $|A|/g_{||} = |B|/g_\perp$, a spectrum of the form as given in fig. 2.3 is obtained. The mean values of $H_\perp(M_I)$ and $H_{||}(M_I)$ are represented by $H_\perp^0$ and $H_{||}^0$ resp., and $\Delta H^0 = H_\perp^0 - H_{||}^0$.

It may be seen from fig. 2.3 that both a higher degree of anisotropy and a smaller hyperfine splitting give rise to a stronger overlap of the bands, which obscures a number of the $2(2I + 1)$ bands.

The spin Hamiltonian used in this discussion only takes into account the
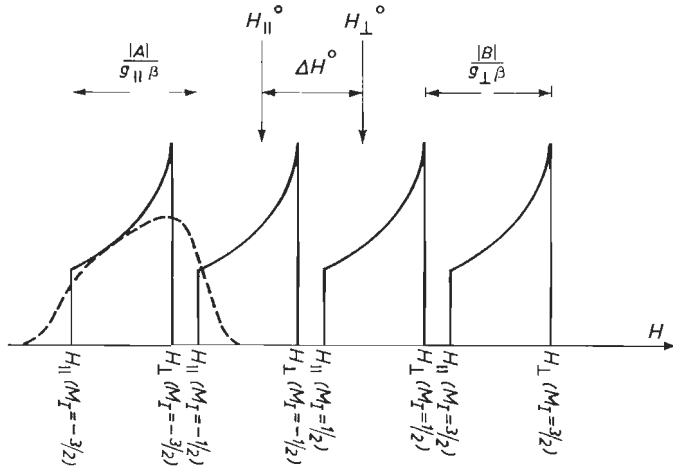
Fig. 2.3. ESR spectrum according to eq. (2.11) for $g_\parallel > g_\perp$, $I = 3/2$ and $|A|/g_\parallel = |B|/g_\perp$.

effects caused by the nearest neighbours of the unpaired electron of the para-magnetic centre. It can be imagined that the next-nearest neighbours have also an — albeit appreciably weaker — influence on the resonance spectrum. In a glass the influence of the next-nearest neighbours will differ from centre to centre. This effect gives rise to a broadening of the theoretical line shape given by eq. (2.11), which is represented by the dashed curve in fig. 2.3.

<div align="center">REFERENCES</div>

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3. COLOUR CENTRES IN ALKALI-BORATE GLASSE

3.1. Introduction

Optical-absorption spectra in the range 1-5 eV for irradiated alkali-borate glasses were first reported by Yokota [1]), who showed the difference in spectra between lithium-, sodium-, potassium- and rubidium-borate glasses at the diborate composition ($M_2^I O.2B_2O_3$). He interpreted the different colour centres in terms of oxygen-ion vacancies of bridging and non-bridging oxygen ions.

The studies on alkali-borate glasses by Ferguson [2]) and on calcium-alumino-borate (cabal) glasses by Bishay [3]) give no new information or interpretation of the colour centres in the pure alkali- or alkaline-earth-borate glasses. Both workers studied the effect of small amounts of deliberately added impurities such as Fe, Ce, Mn, V, Co, Cr, Sb, Ni, Mo [2]) and Dy, Eu, La, Gd, Nd, Tl, Ti, Ge, As [3]) on the intrinsic colour centres and the formation of new types of centres. In both papers the effects were investigated by means of optical-absorption spectra in the range 1 - 6 eV.

In a more recent paper [4]) Bishay and Ferguson showed the influence of the amount of alkali oxide on the optical-absorption bands in glasses of the composition $xM_2^I O.Al_2O_3.4 \cdot 5 B_2O_3$. They resolved the overlapping bands by means of a computer method, assuming each band to be Gaussian. Electron-spin-resonance measurements in irradiated glasses containing boron were first reported by Yasaitis and Smaller [5]). They observed with their 375-Mc/s ESR equipment in a number of irradiated borosilicate glasses a four-lines spectrum with a separation of 10 to 15 gauss between each two lines, which spectrum they attributed to the hyperfine interaction of B^{11} nuclei, (spin = 3/2) with the defect centres. The more recent papers of Nakai [6]), Karapetyan and Yudin [7]) and Sook Lee and Bray [8,9]) on ESR studies of irradiated borate glasses will be discussed in detail in a following section.

So far no paper has been published which combines optical with ESR investigations of colour centres in borate glasses. In the following sections such combined investigations will be described.

3.2. The structure of alkali-borate glasses [10])

3.2.1. *Introduction*

The radiation-induced colouration of solids is attributed to certain defects in the structural units of these solids. On the one hand a study of these defects will give information about the structure of the solids, conversely a knowledge of the structure of solids will lead to a better understanding of the structure of the induced colour centres.

3.2.2. *Definitions*

In the discussion of the borate-glass structure a number of quantities are used, which will be defined in this section.

The composition of the glasses will be represented in mol. fractions

$$x M_2^I O. (1 - x) B_2O_3.$$
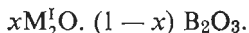
It is generally accepted that the boron ions in boric-oxide glass have a triangular coordination of oxygen ions. In alkali-borate glasses the excess oxygen ions introduced by the alkali oxide may cause a certain number of boron ions to adopt a tetrahedral coordination or may be taken up as non-bridging oxygen ions, in a way analogous to that in the silicate glasses.

If x_4 is the fraction of the x mol. M_2O which gives rise to the formation of BO_4 groups it follows that $(1 - x_4) x$ mol. M_2O gives rise to the formation of non-bridging oxygen ions in the glass network. The fraction of boron ions with a tetrahedral coordination of oxygen ions is

$$N_4 = x_4 x/(1 - x). \tag{3.1}$$

The mean number of non-bridging oxygen ions per polyhedron is

$$X = (1 - x_4)x/(1 - x) = x/(1 - x) - N_4. \tag{3.2}$$

The mean number of bridging oxygen ions per polyhedron is

$$Y = 3 + N_4 - X. \tag{3.3}$$

The mean number of oxygen ions per polyhedron is

$$Z = X + Y = 3 + N_4. \tag{3.4}$$

3.2.3. *The Warren-Abe theory of the structure*

Biscoe and Warren [11]) concluded from their X-ray experiments with sodium-borate glasses that the mean coordination number of the boron ions increases from 3 to a value between 3 and 4 with increasing amount of sodium oxide. This conclusion has been confirmed by Green [12]) for potassium-borate glasses and recently by Becherer, Brümmer and Herms [13]) for sodium-borate glasses. Abe [14]) proposed certain rules for the structure of alkali-borate glasses, which are based on the change in coordination of boron ions, and the anomalies in certain properties at a composition of about 0·17 mol. alkali oxide and 0·83 mol. boric oxide. These rules are:

(1) BO_4 tetrahedra cannot be bound to each other;

(2) non-bridging oxygen ions occur in BO_3 triangles only and are absent in BO_4 tetrahedra;

(3) each BO_3 triangle cannot be bound to more than *one* BO_4 tetrahedron.
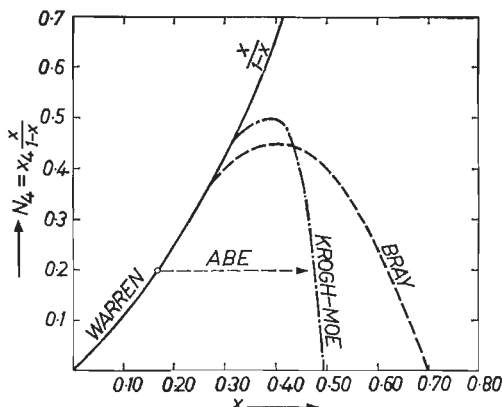
Fig. 3.1. The fraction of boron ions in tetrahedral coordination N_4 as a function of the composition, according to Warren, Abe, Krogh-Moe and Bray.

It follows from these rules that (see also fig. 3.1)

$$\text{for } 0 \leqslant x < \tfrac{1}{6}: \quad x_4 = 1; \quad N_4 = x/(1-x); \quad X = 0; \quad Y = 3 + x/(1-x);$$
$$x = \tfrac{1}{6}: \quad x_4 = 1; \quad N_4 = \tfrac{1}{6} \quad\quad ; \quad X = 0; \quad Y = 3\tfrac{1}{5};$$
$$x > \tfrac{1}{6}: \quad x_4 = (1-x)/5x; \quad N_4 = \tfrac{1}{5}; \quad X = x/(1-x) - \tfrac{1}{6};$$
$$Y = 3\tfrac{2}{5} - x/(1-x). \tag{3.5}$$

According to Abe all the excess oxygen ions are taken up in the form of BO_4 groups in the composition range $0 < x \leqslant \tfrac{1}{6}$. For many years it had been thought that for $x \geqslant \tfrac{1}{6}$ the relative number of boron ions in tetrahedral coordination (N_4) remains constant and all the alkali oxide added in excess of $x = \tfrac{1}{6}$ causes the formation of non-bridging oxygen ions only.

3.2.4. *Results of recent nuclear-magnetic-resonance (NMR) measurements*

The NMR spectra of borate glasses show bands at different frequencies, depending on a different influence of the surroundings of the boron nuclei in BO_3 and BO_4 groups on the local electric field, which interacts with the electrical quadrupole moment of the B^{11}-nuclei (spin $= 3/2$). From the intensity of the fourfold-coordinated boron band in the NMR spectrum, the fraction of boron nuclei in a fourfold coordination has been derived in different ways by Bray et al. [15,16] and Krogh-Moe et al. [17]. These authors concluded that in borate glasses with a low alkali content the excess oxygen ions introduced by the alkali oxide are exclusively used for the formation of BO_4 tetrahedra. Beyond a certain composition (Bray: 0·30 mol. M_2O; Krogh-Moe: 0·33 mol. M_2O) a part of the excess oxygen ions is used for the formation of non-bridging oxygen ions (fig. 3.1). Although the relative values of N_4 derived from the NMR data are accurate, the absolute values of N_4 as a function of the composition must be used with a certain reserve. For $x > 0·40$ the curve given by Krogh-Moe et al.

is not based on NMR data. This may explain the appreciable difference between the shapes of Krogh-Moe's and Bray's curves in this range. For $x < 0.40$ both curves show a similar shape.

The semi-quantitative character of the experimental values of N_4 has a great influence on the reliablity of the values of x at which N_4 starts to deviate from the theoretically attainable value as given by eq. (3.1) in which is substituted $x_4 = 1$. This value of x is very important in relation to the rigidity of the network of a borate glass, as beyond this composition a part of the alkali oxide is now taken up in the form of *non-bridging oxygen ions* that *decrease the rigidity* of the network, unlike the BO_4 tetrahedra that increase the rigidity. Many properties that
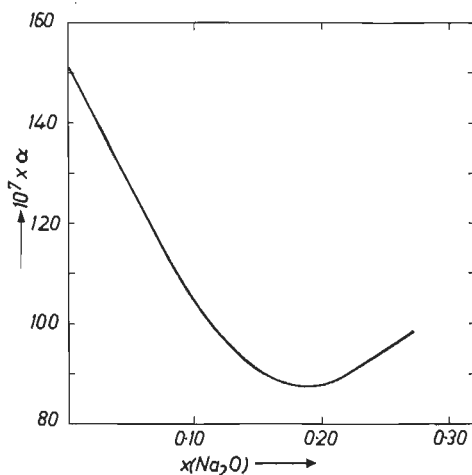
Fig. 3.2. The linear coefficient of expansion α of sodium-borate glasses as a function of the sodium-oxide concentration, after Warren [20]).
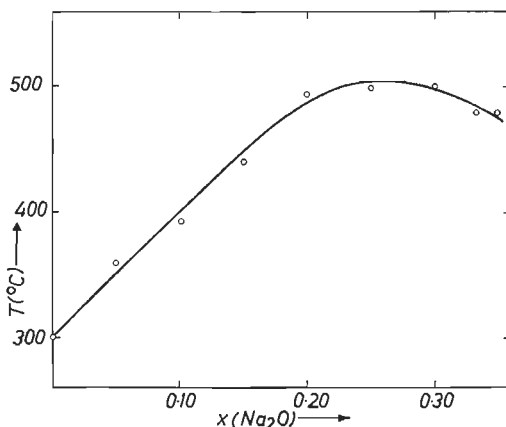
Fig. 3.3. The softening temperature ($\eta = 10^{7.6}$ poises) of sodium-borate glasses as a function of the sodium-oxide concentration, after Eversteyn et al. [21]).

depend on the rigidity of the network show an extreme value at various compositions in the range $0.15 < x < 0.30$ (see e.g. figs 3.2 and 3.3). However, these data do not allow a precise determination of the value of x at which N_4 starts to deviate from the theoretically attainable value of $x/(1 - x)$.

3.2.5. *A hypothesis of the structure of alkali-borate glasses*

The excess oxygen ions introduced by alkali oxide in a borate glass may give rise either to the formation of BO_4 tetrahedra or to the formation of non-bridging oxygen ions. During glass formation, various types of structural units are formed which may consist of the following ions: triangularly coordinated boron ions, tetrahedrally coordinated boron ions, bridging oxygen ions, non-bridging oxygen ions, alkali ions. Five of the possible types of structural units being present in the system are given in fig. 3.4. The amount of each type is determined
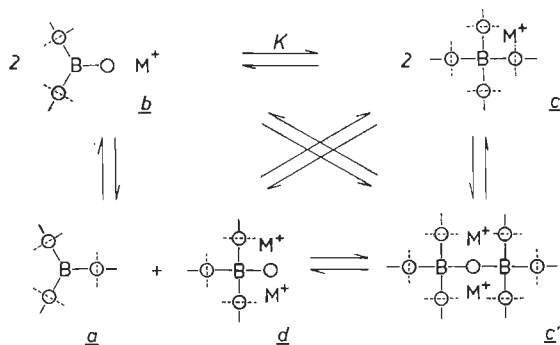
Fig. 3.4. The equilibria between the structural units in an alkali-borate glass.

by a number of equilibria. It seems probable that the structural units c'' and d are appreciably less stable than the structural units b and c'. It is therefore believed that the dominant equilibrium determining the amounts of BO_4 groups and non-bridging oxygen ions, is the one between the units b and c'. Obviously structural units of type a will be found in any alkali-borate glass containing less than 0.50 mol. M_2O. The equilibrium constant K of the equilibrium between the units b and c' can be derived from eqs (3.1) and (3.2):

$$K = N_4/X = x_4/(1 - x_4). \tag{3.6}$$

The magnitude of K is determined by the difference in thermodynamic potential between the two structural units, ΔG, and the applied temperature T:

$$K = \exp(-\Delta G/kT), \tag{3.7}$$

where k is Boltzmann's constant. Hence

$$\ln K = \ln[x_4/(1 - x_4)] = -\Delta G/kT, \tag{3.8}$$

which gives

$$N_4 = x_4 \, x/(1 - x) = [x/(1 - x)] \{1 + \exp (\Delta G/kT)\}^{-1}. \tag{3.9}$$

Using the values of x_4, obtained from Bray's values of N_4 to plot $\ln[x_4/(1 - x_4)]$ versus x (fig. 3.5) it is seen that $\ln K$ is approximately a linear function of x, i.e.

$$\ln K = px + q. \tag{3.10}$$
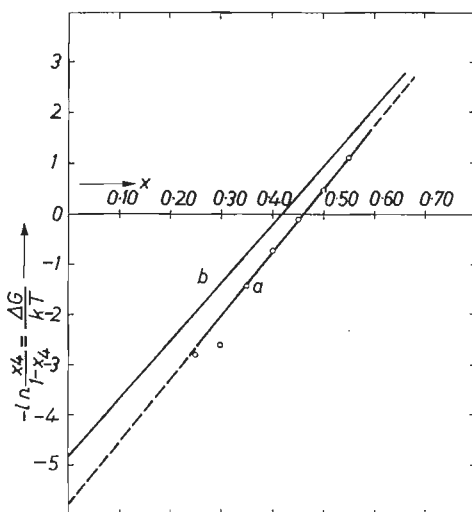
Fig.3.5. $\ln [x_4/(1-x_4)]$ as a function of the composition, according to (a) Bray and (b) this thesis.

As has been already pointed out (cf. sec. 3.2.4), the absolute values of N_4 given by Bray are somewhat doubtful, but the relative values are reliable. No use will therefore be made of the values of the constants p and q derived from Bray's data. Combination of eqs (3.8), (3.9) and (3.10) gives a relation for N_4:

$$N_4 = [x/(1-x)] \, [1 + \exp \{-(px + q)\}]^{-1}. \tag{3.11}$$

It has been mentioned above that the predominant structural units in alkali-borate glasses are a, b and c' of fig. 3.4. The assumption that *only* these units are present leads to the following two structural rules, viz.:

(1) BO_4 tetrahedra cannot be bound to each other;
(2) non-bridging oxygen ions occur in BO_3 triangles only and are absent in BO_4 tetrahedra.

These two rules are identical with Abe's rules (1) and (2). His third rule does not follow from the above equilibrium considerations. *This is the essential difference between Abe's theory of the structure of alkali-borate glasses and the present one* (cf. fig. 3.6).
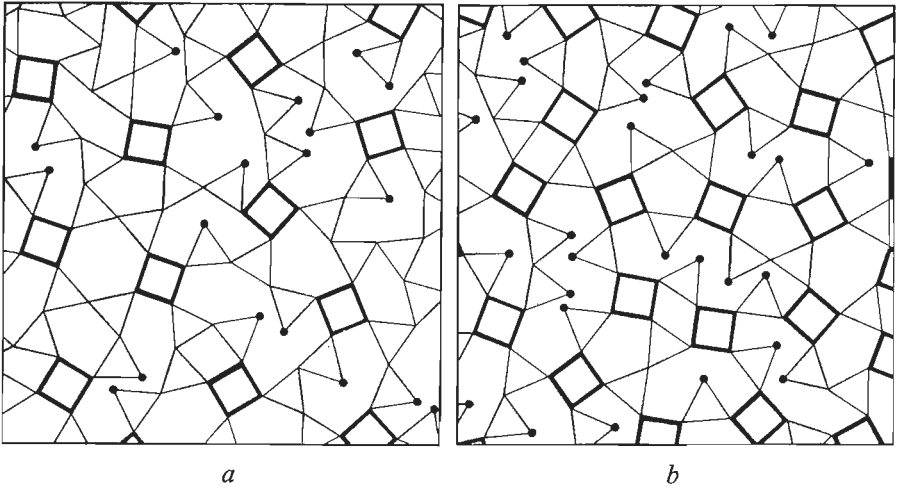
Fig. 3.6. Two-dimensional models of the structure of an alkali-borate glass according to (a) Abe's rules and (b) those presented here.
$\square$ = BO$_4$ group; $\triangle$ = BO$_3$ group; $\bullet$ = non-bridging oxygen ion.
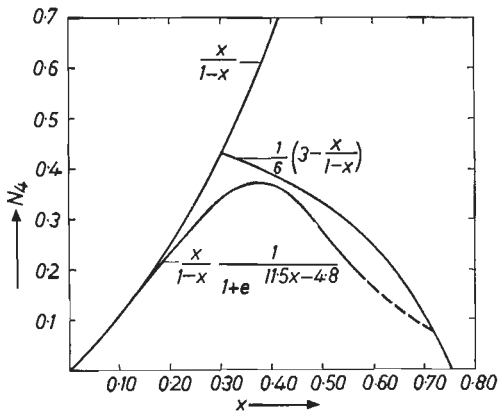
Fig. 3.7. The values of N_4 given by eq. (3.13) compared with the limits for N_4 (eq. (3.12)) according to the hypothesis for the structure of alkali-borate glasses.

It follows from these rules that (see also fig. 3.7)

for $\quad 0 \leqslant x < \frac{3}{10}$: $\quad x_4 = 1$; $\quad N_4 = x/(1-x)$; $\quad X = 0$; $\quad Y = 3 + x/(1-x)$;

for $\quad x = \frac{3}{10}$: $\quad x_4 = 1$; $\quad N_4 = \frac{3}{7}$ $\qquad$; $\quad X = 0$; $\quad Y = 3\frac{3}{7}$;

for $\quad \frac{3}{10} < x < \frac{3}{4}$: $\quad x_4 = \frac{1}{6}[3(1-x)/x-1]$ $\quad$; $\quad N_4 = \frac{1}{6}[3-x/(1-x)]$;
$\qquad\qquad\qquad X = \frac{7}{6}[x/(1-x)-\frac{3}{7}]$ $\quad$; $\quad Y = \frac{4}{3}[3-x/(1-x)]$;

for $\quad x = \frac{3}{4}$: $\quad x_4 = 0$; $\quad N_4 = 0$ $\qquad$; $\quad X = 3$; $\quad Y = 0$. $\qquad$ (3.12)

It has been pointed out in the previous section that it is important to know the composition of the glass where the amount of non-bridging oxygen ions attains

a detectable value or, in other words, where the value of N_4 starts deviating from the highest theoretically attainable value of $x/(1 - x)$. McSwain et al. [18] observed a marked change in the absorption coefficient of borate glasses at about 2000 Å in the composition range of 0·15 - 0·20 mol. M_2O (fig. 3.8). They explain the increase in absorption as being due to the excitation of an elec-
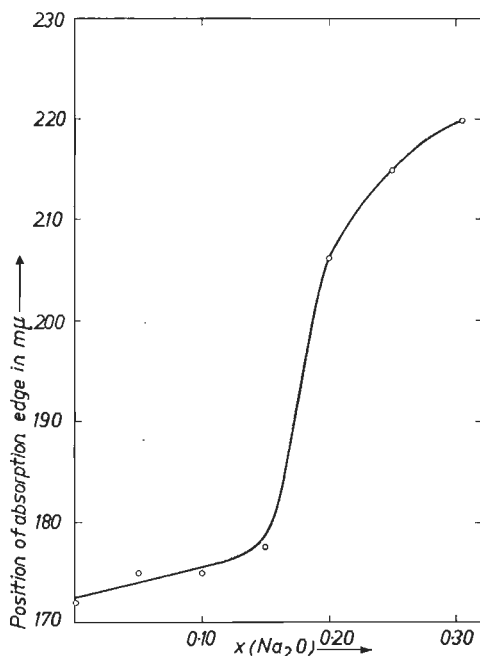
Fig. 3.8. The position of the absorption edge in the u.v. spectrum of sodium-borate glasses as a function of the sodium-oxide concentration, after McSwain et al. [18].

tron of a non-bridging oxygen ion [19]. It may also be concluded from the minimum of the linear-expansion coefficient at a composition $x \approx 0·18$ [20]), that a detectable amount of non-bridging oxygen ions begins to occur at $x \approx 0·15$ (fig. 3.2).

An equation of the form of eq. (3.11), which satisfies the conditions of eq. (3.12) and which is consistent with the initial occurrence of non-bridging oxygen ions at $x = 0·15$ is (fig. 3.5: curve b; fig. 3.7)

$$N_4 = [x/(1 - x)]\{1 + \exp (11·5 \, x - 4·8)\}^{-1}. \qquad (3.13)$$

For $x > 0·60$ this relation is no longer consistent with the shape of the experimental N_4 vs x curve as given by Bray (fig. 3.1). In practice, however, only a few glasses can be prepared in this composition range. The glass-forming ranges of most alkali borates lie between 0 and 0·50 mol. M_2O, where eq. (3.13) is applicable without too large an error.

Properties of borate glasses that depend on the rigidity of the glass network

are determined by the amounts of BO_4 groups and non-bridging oxygen ions. The relative number of boron ions in tetrahedral coordination is given by eq. (3.13). Substitution of eq. (3.13) in eq. (3.2) gives a relation for the mean number of non-bridging oxygen ions per polyhedron:

$$X = [x/(1-x)] \, [1 - \{1 + \exp(11{\cdot}5\, x - 4{\cdot}8)\}^{-1}]. \tag{3.14}$$

The rigidity-dependent properties can be described by a sum of two functions:

$$I_i = F_i(X) + G_i(N_4). \tag{3.15}$$

For certain properties the influence of the number of non-bridging oxygen ions may be dominant, thus the contribution of F_i to I_i is greater than the contribution of G_i. This gives rise to an extreme value of I_i at a composition near $x = 0{\cdot}15$. An example is the linear-expansion coefficient (fig. 3.2). If the influence of the number of BO_4 groups becomes dominant (i.e. if the contribution of G_i to I_i becomes greater than the contribution of F_i) then the extreme value of I_i will be found at a composition nearer to $x = 0{\cdot}38$ (where N_4 versus x shows a maximum). An example of this type of properties is the softening temperature (fig. 3.3).

Certain properties depend only on either the number of non-bridging oxygen ions $(G_i(N_4) = 0)$ or on the number of BO_4 groups $(F_i(X) = 0)$. Examples are respectively the u.v. absorption mentioned previously (fig. 3.8) and the heights of the absorption bands in the infrared spectra of alkali-borate glasses at $9{\cdot}5$ and $10{\cdot}5$ μ, which are attributed to B-O vibrations in BO_4 groups [22,23].

3.3. Experimental results and discussion

3.3.1. *Introduction*

In all the radiation-induced optical-absorption spectra of the borate glasses, given as plots of the optical density α (in cm^{-1}) versus the energy (in eV), the effect of overlapping obscures the various colour-centre bands. It has been pointed out previously (cf. sec. 2.2) that this difficulty can be resolved by computer methods, assuming that each band can be taken to be Gaussian. However, this method can be applied only in the case of highly accurate spectra. Unfortunately the borate-glass spectra are insufficiently accurate, owing to several effects. Differences in dielectric losses of the glasses and in the sensitivity of the equipment, and overlapping effects, give rise to less accurate radiation-induced ESR spectra. Therefore in general only semi-quantitative conclusions may be drawn from the two types of spectra.

3.3.2. *The radiation-induced optical-absorption spectra*

3.3.2.1. The bands in the spectra

In the optical spectra of the borate glasses (figs 3.9-3.14) an absorption band
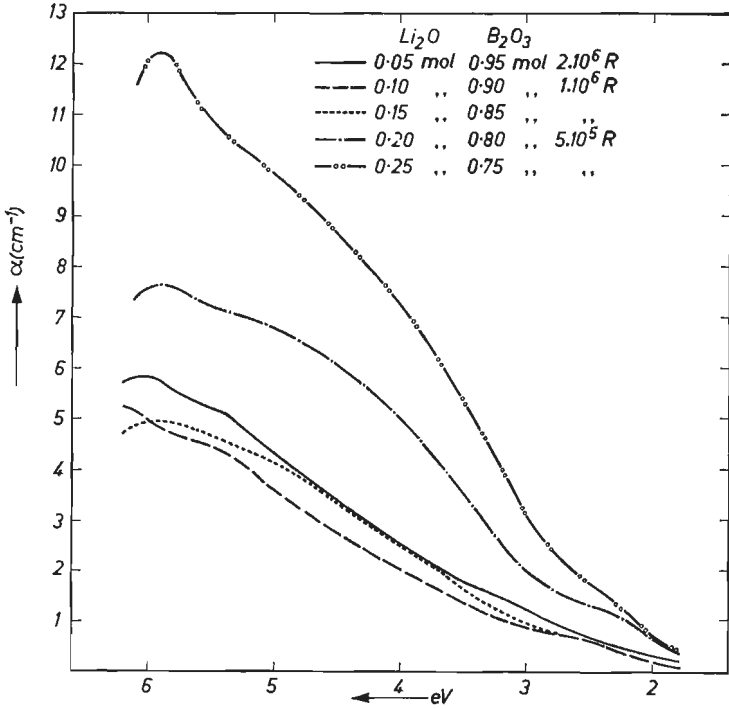
Fig. 3.9. The radiation-induced optical spectra of lithium-borate glasses. Here and in the following figures the radiation dose is given in Röntgen, next to composition of the glasses.
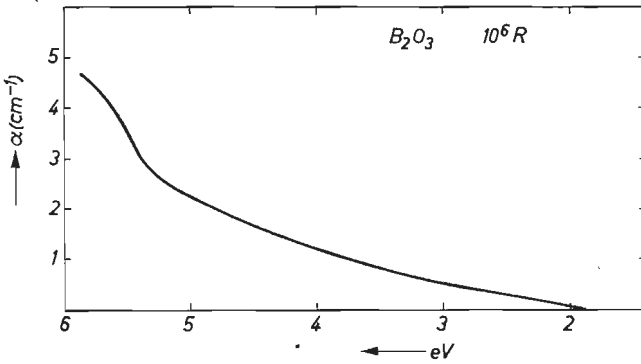
Fig. 3.10. The radiation-induced optical spectrum of fused boric oxide.

is found which shows a change in intensity and energy upon change of alkali ion. This band is found in the region 2·5-1·3 eV (band b_I). The energy of the other bands remains practically unchanged upon change of the alkali ion. These bands are located at about 4 eV (band c_I), 5 eV (band c_{II}) and at an energy
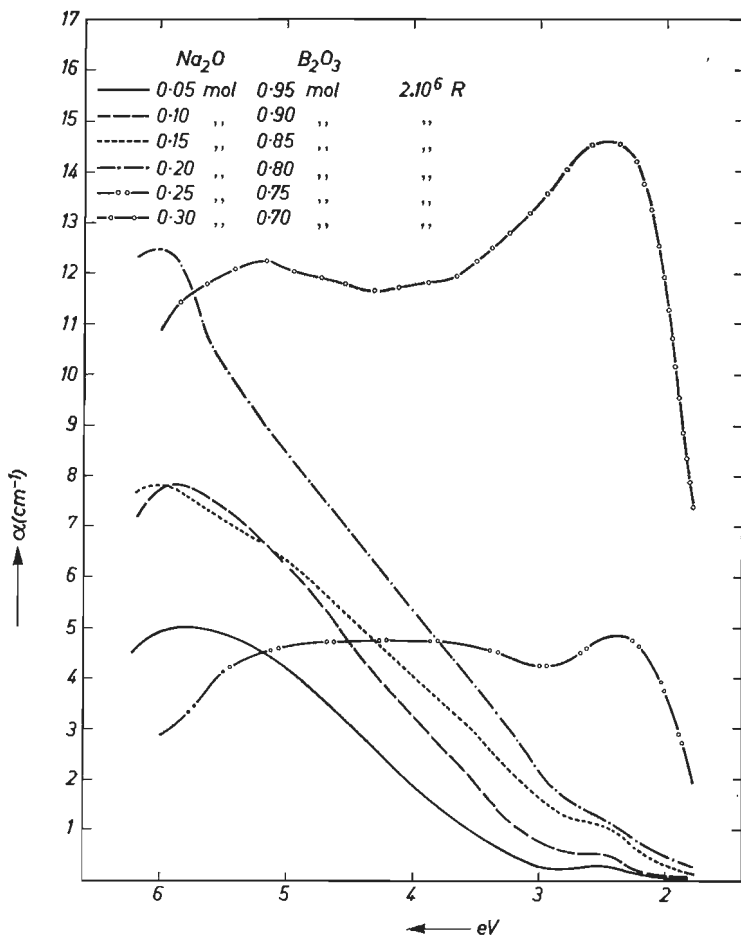
Fig. 3.11. The radiation-induced optical spectra of sodium-borate glasses.

higher than 6 eV (band c_{III}). The choice of the notations b_I, c_I, c_{II} and c_{III} will be explained later.

3.3.2.2. The influence of the composition on the bands

Band b_I (region between 2·5 and 1·3 eV). The occurrence of the b_I-band depends on the composition and the temperature (table I).

Lithium-borate glasses could be obtained in the composition range $0 \leqslant x < 0·45$. However, in the region $0·30 < x < 0·45$ the glasses devitrify on the normal treatment of annealing. To obtain glasses in this composition range it was necessary to quench the melt very rapidly. It was impossible to prepare samples for optical

TABLE I

The influence of the composition and the temperature on the occurrence and the energy of the b_I-band

alkali ion	room temperature		liquid-nitrogen temperature	
	band energy (eV)	appears at x	band energy (eV)	appears at x
Li$^+$	?	0·30	?	?
Na$^+$	2·4	0·25	2·2	0·25
K$^+$	1·95	0·25	1·75	0·25
Rb$^+$	1·75	0·25	1·5	0·20
Cs$^+$	1·5	0·30	1·3	0·15

measurements from these unannealed glasses. Optical spectra of the lithium-borate glasses could therefore only be measured in the composition range $0 \leqslant x < 0\cdot25$ (fig. 3.9). In this composition range no b_I-band was found. It can be concluded from visual inspection of the colour of the irradiated samples in the range $0\cdot30 < x < 0\cdot45$ that the b_I-band is present here.
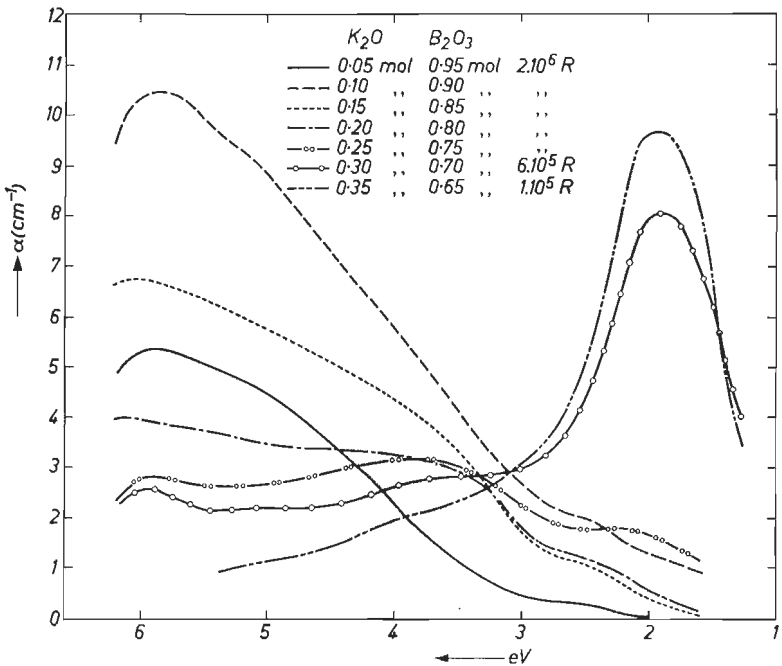
Fig. 3.12. The radiation-induced optical spectra of potassium-borate glasses.
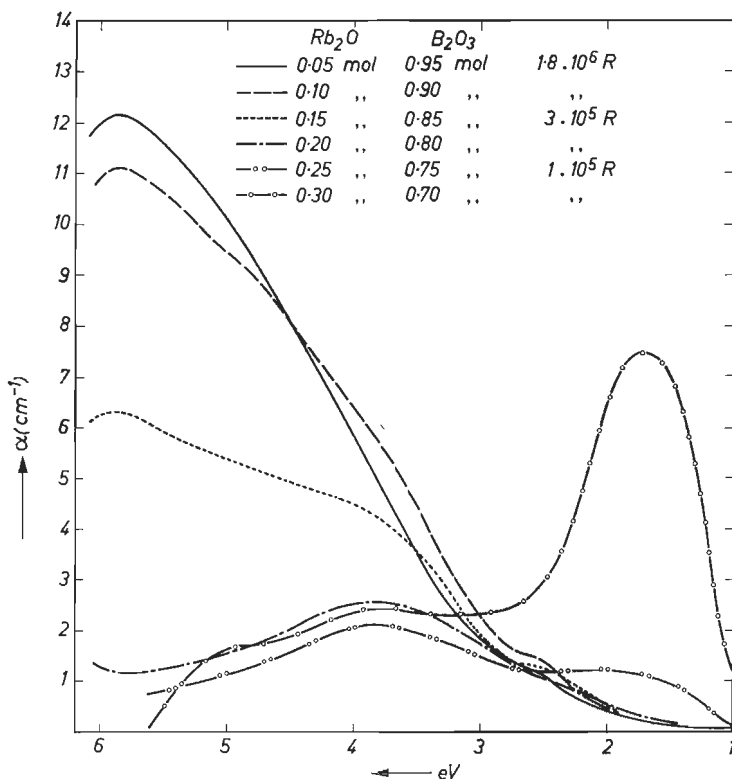
Fig. 3.13. The radiation-induced optical spectra of rubidium-borate glasses.

Samples of the annealed alkali-borate glasses were irradiated and measured at 78 °K. Then the samples were allowed to warm up to room temperature and were measured again. The ratio of the peak heights of the b_I-band measured at these two temperatures is given in table II. Since all the values of a_{298}/a_{78} are found to be much smaller than unity, it may be concluded that the b_I-band is more stable at low temperatures.

TABLE II

The ratios a_{298}/a_{78} of the heights of the b_I-band at 298 °K and 78 °K

alkali ion \ x	0·15	0·20	0·25	0·30	0·35
Li+	—	—	—	?	?
Na+	—	—	0.13	0·20	?
K+	—	—	0·025	0·083	0·33
Rb+	—	0	0·014	0·044	0·067
Cs+	0	0	0·000	0·025	?
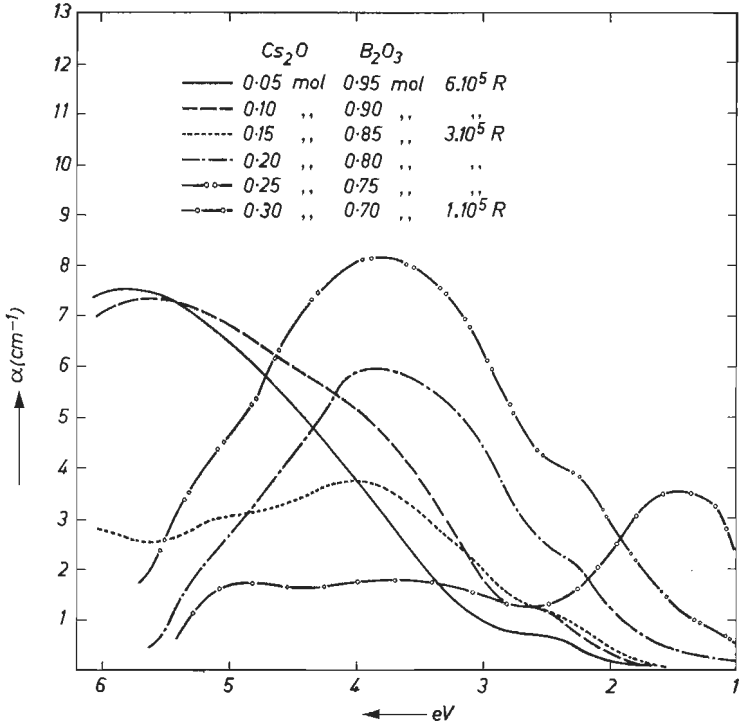
Fig. 3.14. The radiation-induced optical spectra of caesium-borate glasses.

In the cases where $\alpha_{298} = 0$ and $\alpha_{78} = 0$ the ratio is represented by a dash. If only $\alpha_{298} = 0$, then the ratio is represented by a 0. The ratio α_{298}/α_{78} for lithium-borate glasses at the compositions $x \geqslant 0 \cdot 30$ is not known (represented by ?). The trends in the stability of the b_I-band centres are shown in table II: the number of stable colour centres is increased by

(a) increasing the amount of alkali oxide,

(b) increasing the *field strength* *) of the alkali ion.

Furthermore it is seen in table I that with the increase of the field strength the limit of the composition of the glasses, which show the b_I-band at liquid-nitrogen temperature, shifts to higher values of x.

Another important feature of the b_I-band is the approximately linear relationship between the field strength of the applied alkali ions and the band energy E_{max} (fig. 3.15). A lowering of the temperature from 298 to 78 °K causes a

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*) The field strength of an ion is defined as $2z/a^2$, where 2 and z represent the charges of the oxygen ion and the metal ion involved, respectively, and a represents the distance in Å between the centres of the two ions [24].
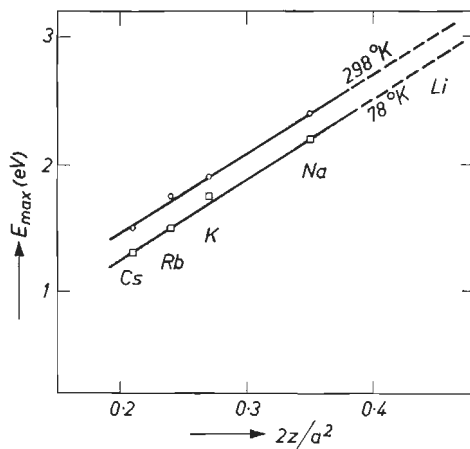
Fig. 3.15. The relationship between the field strength $2z/a^2$ of the alkali ion and the location of the maximum (E_{max}) of the b_I-band in an alkali-borate glass.

practically constant decrease of the band energy of 0·2 eV.

The provisional conclusion is that the alkali ions are involved in both the formation and the structure of the colour centres that cause the b_I-band.

Band c_I (3·8 eV). The c_I-band is practically absent in glasses with a very low alkali-oxide constant ($x < 0.05$), but is found for all other compositions. The band energy is practically not influenced by a change of either the concentration or the type of alkali ion. It seems justified to conclude that the rate of formation rises with the field strength of the alkali ion. The c_I-band appears to be rather broad and is overlapped by neighbouring bands in all the spectra obtained. The values of the ratio a_{298}/a_{78} are therefore not very accurate. However, it may be concluded from the fact that these values are all of the same order of magnitude that the concentration and the nature of alkali oxide do not affect this ratio (table III). As the values of a_{298}/a_{78} are smaller than unity it can be concluded that the b_I-band centres are more stable at lower temperatures.

TABLE III

The ratios a_{298}/a_{78} of the heights of the c_I-band at 298 °K and 78 °K

alkali ion \ x	0·05	0·10	0·15	0·20	0·25	0·30	0·35
Li^+	—	—	—	0·35	0·25	?	?
Na^+	—	—	0·16	0·18	0·17	0·20	?
K^+	—	0·23	0·20	0·18	0·15	0·13	0·25
Rb^+	—	0·35	0·20	0·29	0·25	0·13	0·15
Cs^+	—	0·25	0·24	0·30	0·33	0·17	?

From the absence of an influence of the alkali ions on the c_I-band energy and the ratio α_{298}/α_{78} it may be concluded that the colour centres causing this band contain only boron and oxygen ions. The alkali ions are involved in the formation of these centres, as the intensity of the c_I-band above a certain radiation dose does depend on the alkali ion (cf. figs 3.9, 3.11, 3.12, 3.13 and 3.14).

Band c_{II} (≈ 5 eV). It is difficult to make definite statements about the behaviour of the c_{II}-band as a function of the concentration or the nature of the alkali oxide used, owing to the strong overlap with the c_{III}-band (>6 eV) in the glasses with a low alkali-oxide content and with the c_I-band in the glasses with a high alkali-oxide content. The band energy seems practically independent of the concentration or nature of the alkali oxide used. It may therefore be assumed that the alkali ions do not form part of the colour centres causing the c_{II}-band.

Band c_{III} (>6 eV). As pointed out above (cf. sec. 2.2), the optical results near 6 eV must be interpreted with a certain reserve. However, the incline of the c_{III}-band, which is already observed near 5 eV, allows rough conclusions to be drawn concerning its intensity. The band energy could not be estimated, but the curves suggest that it is independent of the nature or concentration of the alkali ions.

The intensity of the c_{III}-band increases with the concentration for each alkali ion up to a certain value of x (table IV) and then decreases again rapidly (cf. figs 3.9, 3.11, 3.12, 3.13, 3.14).

TABLE IV

Concentration of alkali oxide in alkali-borate glasses at which the c_{III}-band is maximum

	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
x	>0.25	0.20	0.10	0.10	0.10

It therefore seems justifiable to conclude for the moment that the alkali ions are involved in the formation of the colour centres causing the c_{III}-band, but they do not actually form part of these centres.

Summarising it may be concluded that four major types of colour centres can be detected by means of optical spectroscopy in the range 2000-12000 Å (6 - 1 eV). In one type (b_I-band) the alkali ions take part in the formation as well as in the structure of the centres while in the other types (c_I-, c_{II}- and c_{III}-bands) the alkali ions are involved in the formation of the centres, but do not form part of their structure.

3.3.3. *The radiation-induced ESR spectra*

3.3.3.1. The bands in the spectra

In glasses with a low alkali-oxide content and in B_2O_3 glass a six-lines spectrum has been observed (see figs 3.16 and 3.17; the ESR spectra are recorded as first-derivative curves). The bands 2, 3, 4 and 5 are approximately equally spaced and show equal widths. Band 1 is broader and the spacing between 1 and 2 is larger. Band 6 is apparently narrower than bands 2, 3, 4 and 5 and the spacing between 5 and 6 is also smaller. The conclusion is that the bands 2, 3, 4 and 5 arise from the hyperfine interaction of a nucleus with a spin $= 3/2$. The hyperfine splitting of this resonance in B_2O_3 glasses is due to the isotope B^{11}, as may be concluded from table V.
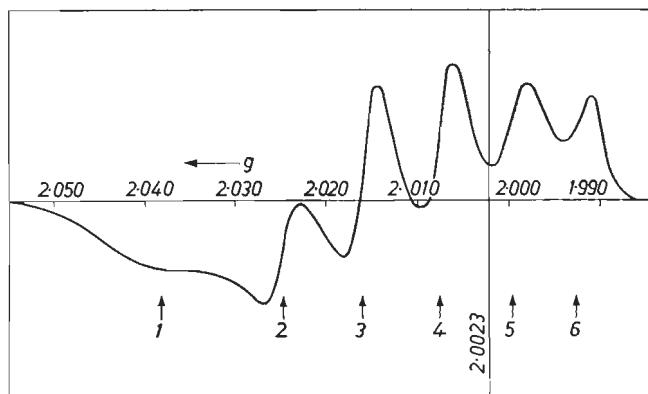
Fig. 3.16. The radiation-induced ESR spectrum of fused boric oxide.
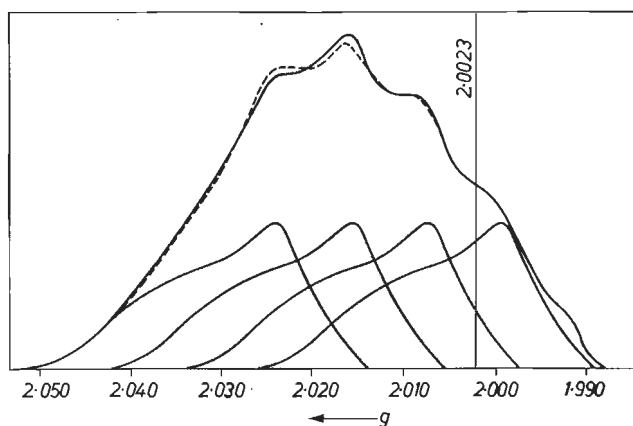
Fig. 3.17. Resolved radiation-induced ESR spectrum of fused boric oxide. Full curve: observed spectrum (integrated spectrum of fig. 3.16); dashed curve: sum of the four equally spaced, anisotropic bands.

TABLE V

Abundance of the isotopes in a B_2O_3 glass

isotope	natural abundance (%)	at. % in glass	nuclear spin
H^1	99·9	1	1/2
B^{10}	18·8	7·4	3
B^{11}	81·2	32·2	3/2
O^{16}	99·76	59·25	—
O^{17}	0·04	0·02	5/2
O^{18}	0·20	0·12	—

The mean g-factor of the four bands 2, 3, 4 and 5 is about 2·012, which is larger than the free-electron value ($g = 2·0023$). The paramagnetic centre causing this four-band spectrum may therefore be characterized as an electron-hole centre adjacent to a B^{11} nucleus. The single band 6 with $g = 1·993$ (smaller than 2·0023) may be assumed to be due to an electron centre. Band 1 will be discussed later.

Glasses with a high alkali content show a marked four-band spectrum with a mean g-factor of 2·010 (figs 3.18, 3.19, 3.20). In a rubidium-borate glass with $x = 0·40$ this spectrum becomes vague (fig. 3.21). In a caesium-borate glass with $x = 0·40$ the four-band spectrum has disappeared totally, leaving a relatively broad, symmetrical band without hyperfine structure ($g = 2·014$; fig. 3.22).

The glasses with a medium alkali-oxide content show ESR spectra which are mixtures of spectra of a glass with a low and a high alkali-oxide content (see e.g. fig. 3.20; composition: 0·30 K_2O. 0·70 B_2O_3).

3.3.3.2. The spectrum of B_2O_3 glass

The ESR spectrum of irradiated B_2O_3 glass should be discussed first, as it is present in all the glasses with a low alkali-oxide content.

Band 6 ($g=1·993$). As pointed out in the previous section the spacing between the single band 6 (fig. 3.16) and band 5 is smaller than the hyperfine splitting between the four equally spaced bands 2, 3, 4 and 5. Furthermore, it may be seen from the various spectra showing this band that its half-width is smaller than that of each of the four bands 2, 3, 4 and 5. It may thus be concluded that band 6 is not related to the colour centres causing the four hyperfine bands. This is in disagreement with the assignments of Sook Lee and Bray [8]), who assumed the bands 3, 4, 5 and 6 to be due to the hyperfine interaction of a hole with a B^{11} nucleus (table VII).

The present assignment of the band with $g = 1·993$ agrees with Nakai's [6]) conclusion that this band is due to another type of colour centres. However, Nakai's
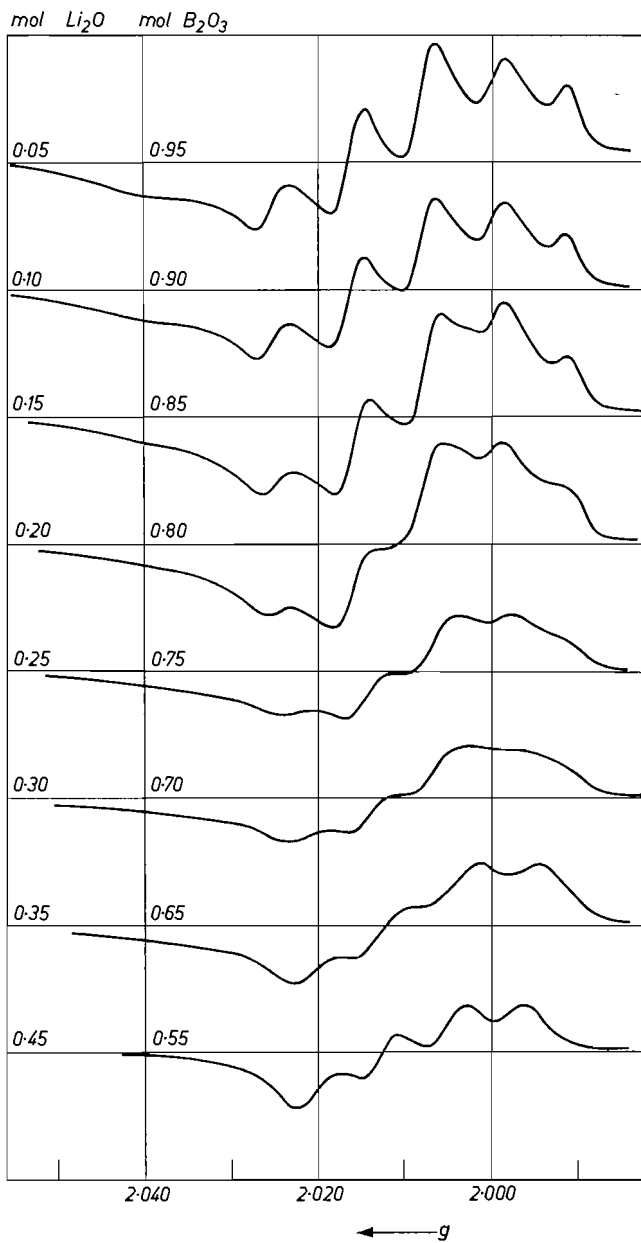
Fig. 3.18. The radiation-induced ESR spectra of lithium-borate glasses.
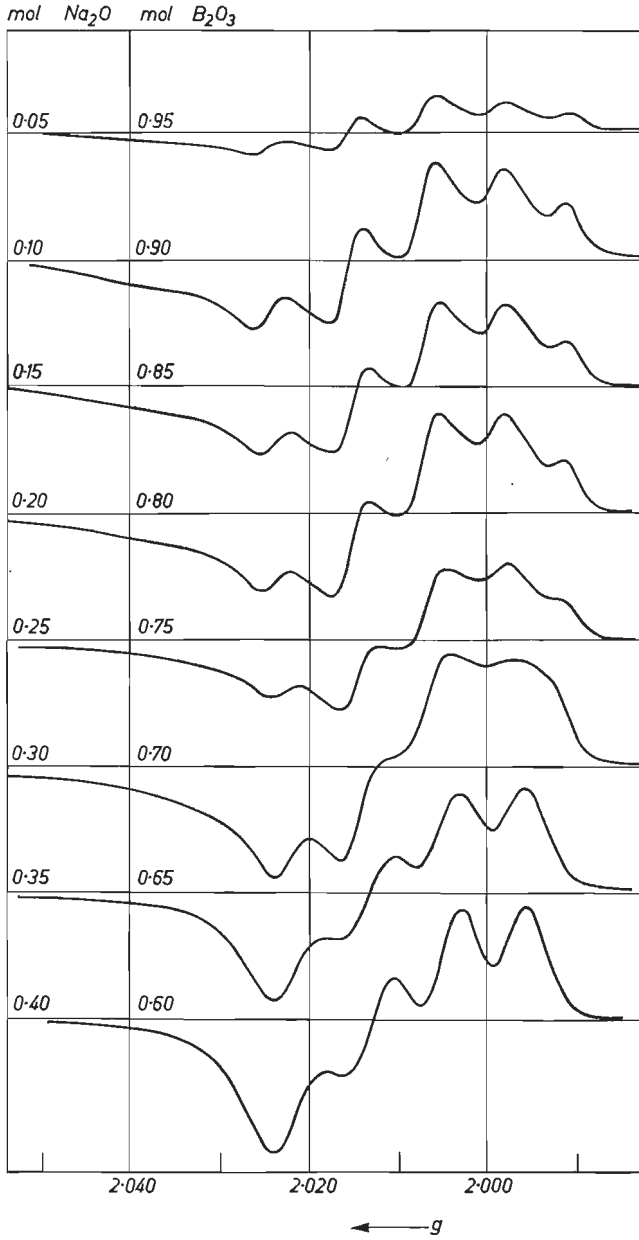
Fig. 3.19. The radiation-induced ESR spectra of sodium-borate glasses.
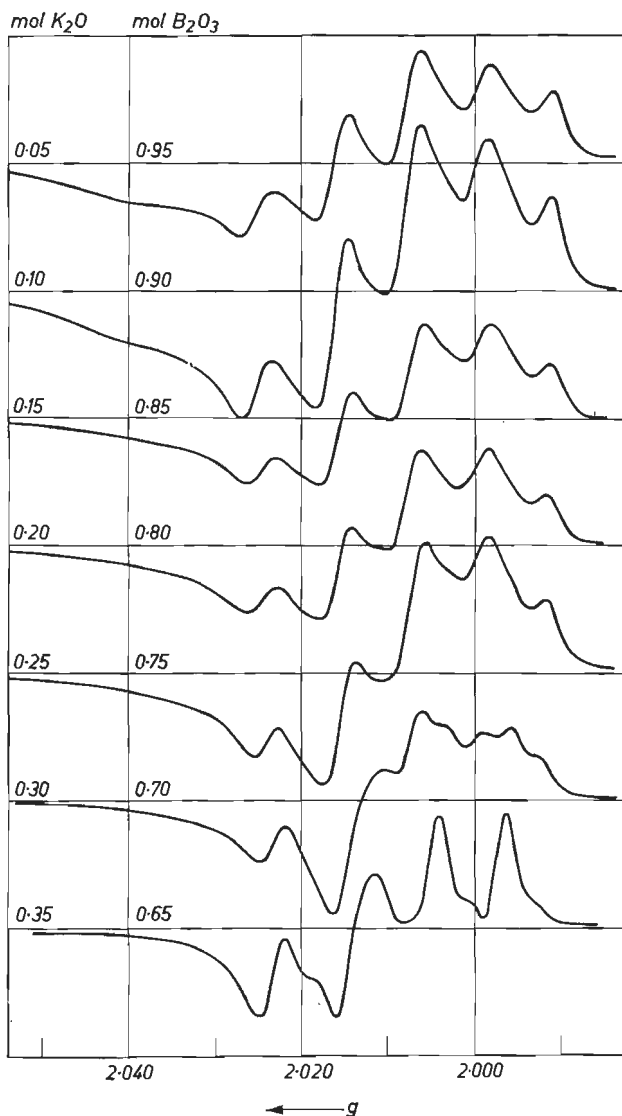
Fig. 3.20. The radiation-induced ESR spectra of potassium-borate glasses.

assignment of this band to a centre containing a hydrogen ion could not be confirmed by a number of experiments described below.

Boric-oxide glass has been prepared in different ways:

(a) from H_3BO_3 (p.a. "Merck"), melted at 1300 °C in air;
(b) from H_3BO_3, obtained from pure trimethyl borate by hydrolysis, melted at 1300 °C in air *);

*) This boric acid has been prepared by Dr W. Kwestroo.
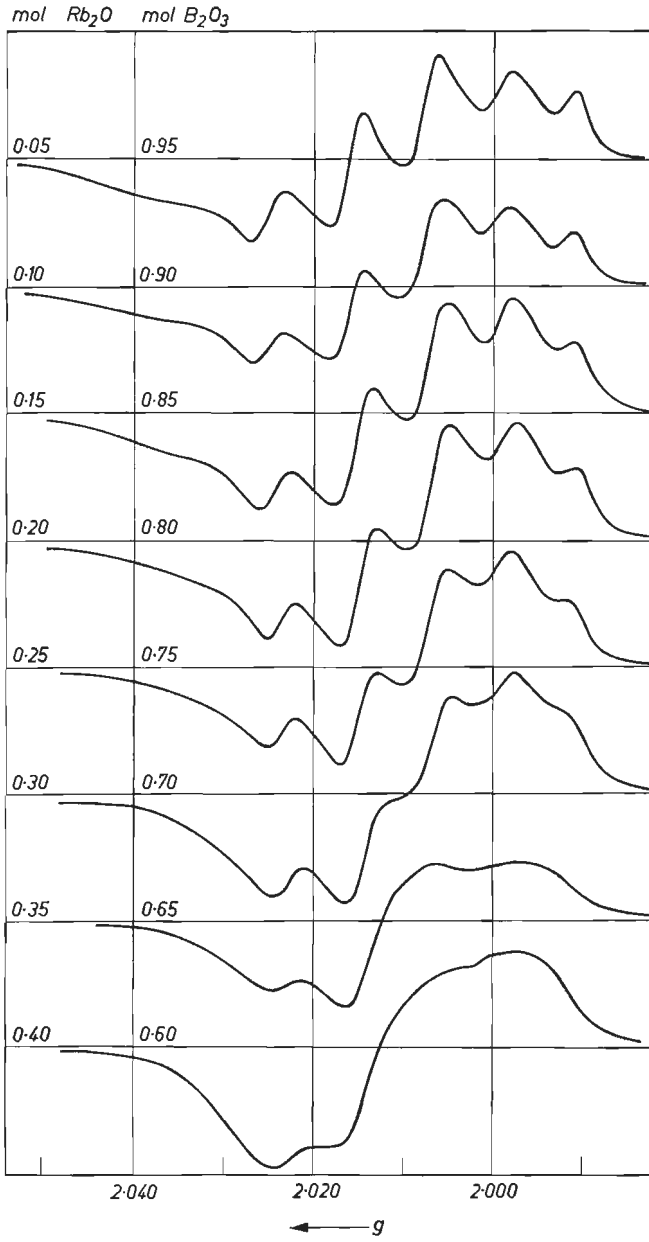
Fig. 3.21. The radiation-induced ESR spectra of rubidium-borate glasses.
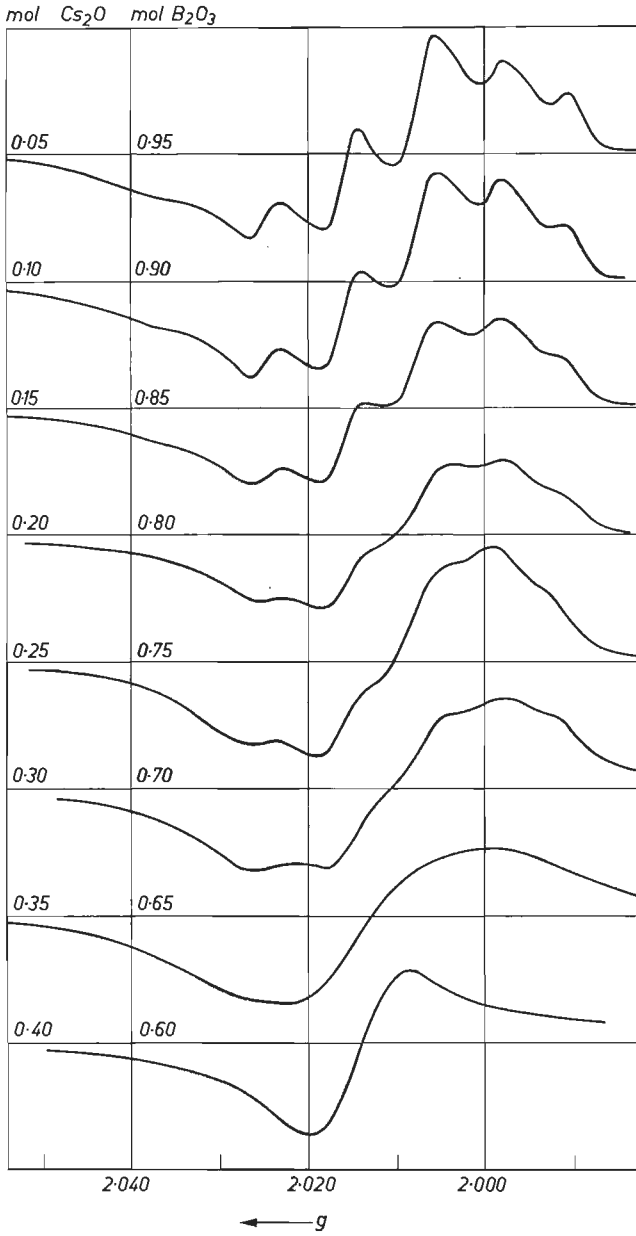
Fig. 3.22. The radiation-induced ESR spectra of caesium-borate glasses.

(c) from a mixture of approximately equal amounts of H_3BO_3 and D_3BO_3, melted at 1300 °C in air;

(d) from H_3BO_3 (p.a. "Merck"), melted at 1300 °C, dry nitrogen bubbled through for two hours;

(e) from H_3BO_3 (p.a. "Merck"), melted at 250 °C; Milberg, Belitz and Silver [25] showed that at this temperature a "B_2O_3 glass" is obtained with about 25-35 mol. % H_2O;

(f) from H_3BO_3 (p.a. "Merck"), melted at 1300 °C and fired at 700 °C in vacuum.

The ESR spectra (fig. 3.23) of the glasses (a), (c) and (d) are independent of the different methods of preparation. The shape of the spectrum of glass (e), which contains about 30 mol. % H_2O is comparable to that of the lithium- and sodium-
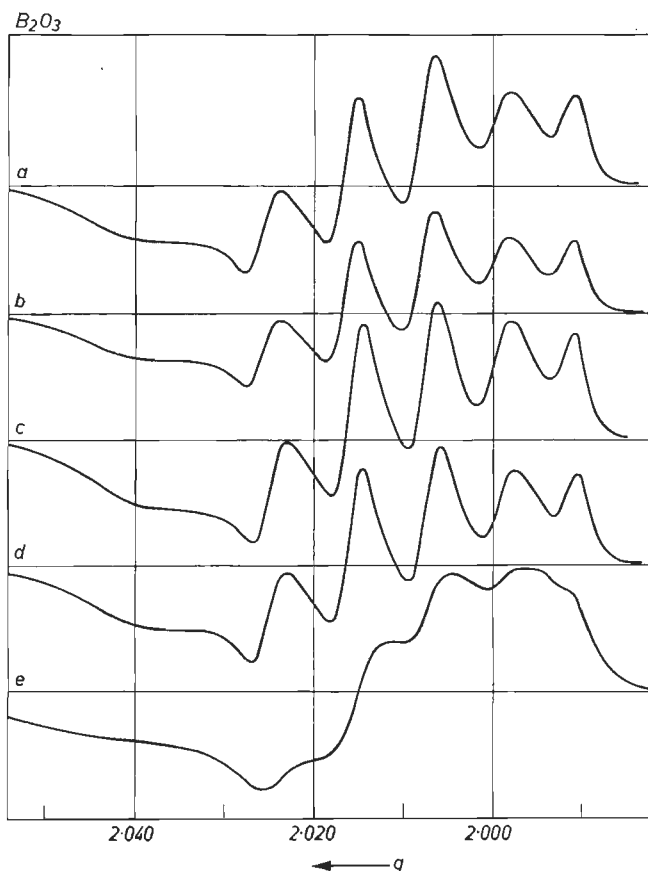
Fig. 3.23. The radiation-induced ESR spectra of fused boric oxide, prepared from:
(a) H_3BO_3 (p.a. "Merck"), melted at 1300 °C in air;
(b) H_3BO_3 obtained from pure trimethyl borate by hydrolysis, melted at 1300 °C in air;
(c) a mixture of approximately equal amounts of H_3BO_3 and D_3BO_3, melted at 1300 °C in air;
(d) H_3BO_3 (p.a. "Merck"), melted at 1300 °C in a dry nitrogen atmosphere;
(e) H_3BO_3 (p.a. "Merck"), melted at 250 °C; this glass contains about 25-35 mol. % H_2O.

borate glasses with $x = 0.30$. It is therefore believed that band 6 is due to colour centres which contain neither alkali nor hydrogen ions.

The spectrum of glass (f) which was dehydrated in vacuum, appears to be of the same shape as that of glass (a), but the intensity of all bands is about 20 to 30 times less. Furthermore, it could be established that the ESR bands of B_2O_3 glass (a) are about 10 times as weak as the bands of a potassium-borate glass with 0.10 mol. K_2O. Apparently the hydrogen ions are involved in the formation of the centres causing the ESR bands, in a way similar to that of the alkali ions. Hyperfine interaction between the colour centres and the hydrogen or alkali ions were never observed. Hence, neither hydrogen nor alkali ions form part of these centres.

The influence of minor amounts of impurities which are always present in the batch materials have been checked with a glass (b) (fig. 3.23) prepared from H_3BO_3 obtained from trimethyl borate by hydrolysis. This boric acid cannot contain the same amounts of the same impurities as "Merck's" boric acid (table VI).

TABLE VI

Impurities in "Merck's" boric acid (p.a.)

impurity	maximum content in weight %
Cl'	0.0005
SO_4''	0.0002
PO_4'''	0.001
heavy metals such as $Pb^{++(++)}$	0.0008
$Fe^{++(+)}$	0.0002
Ca^{++}	0.002

In spite of differences in impurity content, the ESR spectra of glasses (a) and (b) are identical. It is therefore believed that impurities do not form part of colour centres in borate glasses.

It may be concluded that band 6 ($g = 1.993$) is due to a colour centre which does contain neither hydrogen nor impurity ions, but only boron and oxygen ions.

It may similarly be concluded from the above that the bands 1, 2, 3, 4 and 5 are caused by colour centres containing *boron* and *oxygen* ions only. A more detailed discussion of these bands follows.

The bands 2, 3, 4 *and* 5. As pointed out in sec. 3.3.3.1 the four bands with a mean $g = 2.012$ may be attributed to the hyperfine-splitting action of a B^{11}

nucleus adjacent to the colour centre (fig. 3.16). The integrated spectrum of irradiated pure B_2O_3 glass is given by the full line in fig. 3.17. This spectrum could be resolved by a trial-and-error method into four equally spaced and shaped bands, apart from the small band 6 at $g = 1\cdot993$ discussed previously. The sum (dashed curve) of these four bands deviates somewhat from the experimentally observed curve (full line), which may be explained in terms of uncertainties partly present in the experimental curve and partly introduced by the trial-and-error method.

Band 1 ($g = 2\cdot038$) appears to be due to the anisotropy of the g-factor of the colour centres which cause the four bands 2, 3, 4 and 5. These four bands may be represented by eq. (2.12) (cf. sec. 2.3.2) if it is assumed additionally that
(1) $|A|/g_{||} = |B|/g_{\perp} \approx \Delta H^0$ (fig. 2.3),
(2) line broadening occurs owing to the differences in the surrounding of the centres involved (cf. sec. 2.3.2).
This assignment of the bands in the ESR spectrum of irradiated B_2O_3 glass differs from the one given by Sook Lee and Bray [8] (cf. table VII and figs 3.16 and 3.17). They believed the bands 2, 3, 4, 5 and 6 to be due to the hole centre adjacent to a B^{11} nucleus. An attempt to resolve these bands by trial and error into four equal and equally spaced bands, as has been shown for the bands 1, 2, 3, 4 and 5 (cf. fig. 3.17), has failed.

It may provisionally be concluded that the bands 1, 2, 3, 4 and 5 arise from electron-hole centres which interact with an adjacent B^{11} nucleus, and experience an axially symmetric crystal field (cf. sec. 2.3.2).

TABLE VII

The assignment of the bands in the ESR spectrum of irradiated B_2O_3 glass according to Sook Lee and Bray [8] and to this thesis

band no.	g-factor	Sook Lee and Bray [8]	this thesis
1	$2\cdot038$		$g_{||}(M = -3/2)$
2	$2\cdot025$	$g_{||}(M = -3/2)$	$g_{\perp}(M = -3/2)$
3	$2\cdot016^5$	$g_{\perp}(M = -3/2)$	$g_{\perp}(M = -1/2)$
4	$2\cdot008$	$g_{\perp}(M = -1/2)$	$g_{\perp}(M = 1/2)$
5	$1\cdot999^5$	$g_{\perp}(M = 1/2)$	$g_{\perp}(M = 3/2)$
6	$1\cdot993$	$g_{\perp}(M = 3/2)$	see text

3.3.3.3. The influence of the composition on the spectra

As pointed out in sec. 3.3.3.2, the four-band spectrum in a glass of composi-

tion 0.10 $K_2O.0.90$ B_2O_3 is about ten times as strong as the spectrum of B_2O_3 glass (with approximately 1 mol. $\%$ H_2O).

At higher alkali-oxide concentrations the rather pronounced hyperfine splitting becomes weaker. A further increase of the alkali-oxide content gives rise to the appearance of a four-band spectrum (mean g-value $= 2.010$) which shows no anisotropy. This hyperfine splitting is most pronounced in the potassium-borate glasses (fig. 3.20). In the lithium- and sodium-borate glasses (figs 3.18 and 3.19) the hyperfine bands are somewhat broader. In the rubidium-borate glasses (fig. 3.21) the hyperfine splitting of the isotropic four-band spectrum is no longer well resolved. In a caesium-borate glass with $x = 0.35$ (fig. 3.22) these bands are still faintly visible, but in the glass with $x = 0.40$ one broad band without hyperfine structure is found, with a g-factor $= 2.014$. In the alkali-borate glasses with a composition $x > 0.30$ the four anisotropic bands could not be detected, except in a potassium-borate glass, where the four isotropic bands are well resolved and the anisotropic bands are still faintly visible (fig. 3.20).

In the series of potassium-borate glasses the change of the spectrum with the composition may be observed most clearly. The hyperfine splitting of the four anisotropic bands decreases somewhat. At $x = 0.30$ a mixture of approximately equally strong anisotropic and isotropic four-band spectra is found. The mean g-factors and the hyperfine splitting of these two spectra differ only slightly. It is therefore believed that the structures of the colour centres that give rise to these two spectra must also be very similar.

A general conclusion to be drawn for the ESR spectra is that the g-factors of the absorption bands are practically unaffected by a change in alkali ion. Moreover, there is no evidence of hyperfine splitting caused by alkali or hydrogen ions. It may therefore be concluded that these ions do not form part of the colour centres causing the ESR-absorption bands.

3.3.4. *Comparison and discussion of the optical- and ESR-absorption spectra*

3.3.4.1. Introduction

The colour centres may be divided into two groups on the basis of the dependence of the energy of the absorption bands on the alkali ion. The energy of the b_I-band depends strongly on the alkali ion present. The colour centres causing this band will be called alkali-dependent. The energy of the other optical-absorption bands is practically independent of the alkali ion. The colour centres causing these bands will be called alkali-independent, though it should be remarked that the alkali ions in question do have a minor effect.

3.3.4.2. The alkali-dependent colour centres

The energy of the optical b_I-band (2.4-1.3 eV) depends on the alkali ion. A corresponding band in the ESR spectrum has not been found.

A model of the colour centre causing this band should satisfy the following requirements:

(1) it should include an alkali (hydrogen) ion;

(2) since an ESR band is absent, the centre is likely to contain a pair of electrons or holes;

(3) its progenitors must be present in a glass of $x > 0.15-0.25$.

Glasses with $x > 0.15$ contain non-bridging oxygen ions bound to boron ions in triangular coordination. During irradiation the following reaction may take place in such glasses:

b-unit b_I-centre
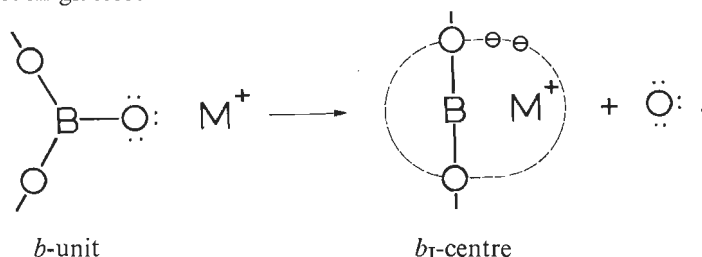
The structure of the b_I-centre is in accordance with the three requirements mentioned above.

In irradiated alkali-silicate glasses Kats and Stevels [26] observed a band in the optical spectrum which increases in intensity with an increase in the alkali-oxide content, in other words with an increase in the number of non-bridging oxygen ions per polyhedron ($=X$). This band is located at 2.07 eV for sodium-silicate glasses and shifts to 1.94 eV for caesium-silicate glasses. These authors assigned this band to colour centres containing a non-bridging oxygen vacancy and an alkali ion [26,27]. This model is very similar to the model proposed here for the b_I-centres.

A fact which may explain the relatively easy formation of the proposed b_I-centres is found in the discussions concerning oxygen-vacancy centres in various types of fused silica. Weeks [28] concluded that in the optical spectra of fused silica without impurities (except hydrogen) two bands may be induced at 2140 Å and 2300 Å, which are attributed to two types of oxygen vacancies which have captured an electron [29]. If fused silica prepared from natural quartz is submitted to the same radiation dose (10^7R . Co^{60}) a band appears at 2200 Å which is about 5 times as strong as the bands at 2140 and 2300 Å. This band has also been attributed to a centre consisting of an oxygen vacancy which has trapped an electron [28]. Hence, the formation of the same amount of these centres requires an appreciably smaller radiation dose in the presence of impurities. It thus seems likely that oxygen vacancies are formed more easily in a glass network upon irradiation where the oxygen ions are bound less tightly to the network owing to the presence of ions other than the original network formers.

3.3.4.3. The alkali-independent colour centres

In the optical spectra the following trend in the intensity of the bands c_I (3·8 eV), c_{II} (5 eV) and c_{III} (>6 eV) is observed. In glasses with a *low* alkali-oxide content the c_{III}-band is the major one, the c_{II}-band being weak and the c_I-band being practically absent. A similar picture is found in pure B_2O_3 glass [2]) (fig. 3.10). With a rise of the concentration of alkali oxide the c_{III}-band decreases and vanishes. This effect could not be verified in the lithium-borate glasses, as samples for optical measurements could not be prepared at the required compositions. In the other alkali-borate glasses the c_I- and c_{II}-band increase as the c_{III}-band decreases; in the sodium-borate glasses the c_{II}-band dominates at a certain composition and in the caesium-borate glasses the c_I-band.

In the ESR spectra, the following trend may be observed. The four anisotropic bands are replaced by four isotropic bands as the alkali-oxide content increases. However, in the rubidium- and caesium-borate glasses these four isotropic bands are not very well resolved and even vanish in the glass of composition 0·40 Cs_2O . 0·60 B_2O_3. In a recent paper Sook Lee and Bray [9]) reported a similar vanishing of the four isotropic bands in a lithium-borate glass of composition 0·65 Li_2O . 0·35 B_2O_3. It is not unlikely therefore that at a certain composition the four isotropic bands in the sodium-, potassium- and rubidium-borate glasses will also vanish, however these glasses could not be prepared with the available quenching technique.

Combining the two observed trends it may be concluded that the c_{III}-band (>6 eV) is connected with the four anisotropic bands, the c_{II}-band (5 eV) with the four isotropic bands and the c_I-band with the unresolved broad single band at $g = 2·014$ as is found in the 0·40 Cs_2O . 0·60 B_2O_3 glass. It is believed that this band is also present as a sort of background in the spectra of caesium-borate glasses (and in the other alkali-borate glasses) at a lower alkali-oxide concentration.

The colour centres causing the four *anisotropic* ESR bands show the following features:
(1) they contain an electron hole ($g = 2·012$);
(2) the number of centres increases with the concentration of the alkali ions (including hydrogen ions) at low concentrations ($x<0·15$);
(3) they contain only one boron nucleus (*four* hyperfine bands);
(4) the crystal field in the environment of the centre is axially symmetrical (anisotropic g-factor);
(5) they contain neither alkali nor hydrogen ions.

In the concentration range mentioned under (2) the unirradiated glass contains structural units of type c' and a (cf. sec. 3.2.5). In this region the number of non-bridging oxygen ions (b-units) is negligibly small. Irradiation may introduce a hole into both units by the following reactions.

c'-unit c-centre

a-unit a-centre
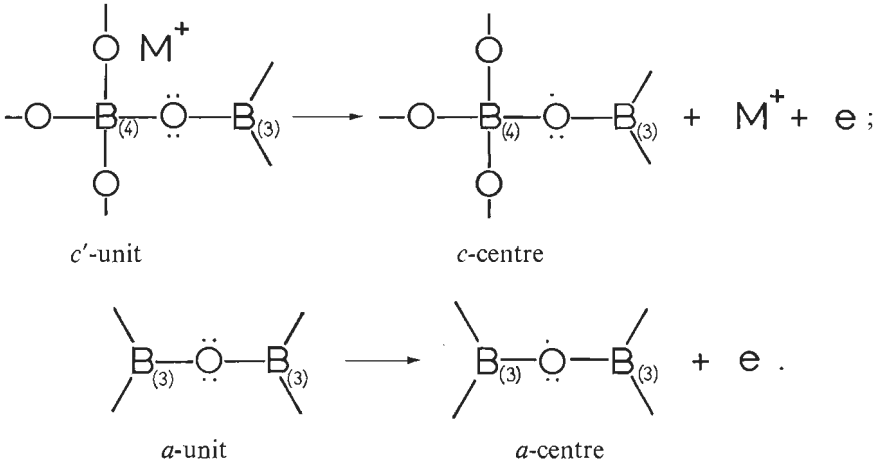
As the a-centre is not neutral, it will be less stable than the c-centre and will readily capture an electron. Moreover, a hole on an oxygen ion between two equivalent boron ions (both are threefold coordinated) as shown in the a-centre will interact with both boron nuclei to the same extent, which means that a hyperfine structure of at least seven bands should be found $(2(3/2 + 3/2) + 1 = 7)$. The c-centre agrees with all the features mentioned above:

ad (1): it contains an electron hole;

ad (2): for small values of x the relative number of boron ions in tetrahedral coordination is given by $N_4 = x/(1 - x)$ (for $x < 0.15$; $x_4 \approx 1$). Thus, an increase in x gives rise to an increase in N_4, which explains the increase in the number of colour centres;

ad (3): the hole is located on an oxygen ion between two non-equivalent boron ions, (a $B_{(4)}$ and a $B_{(3)}$ ion). The hole will be attracted to the $B_{(4)}$ ion as this ion has an excess of negative charge, which explains the hyperfine interaction with one boron nucleus only;

ad (4): if the hole is located on one particular oxygen ion between a $B_{(4)}$ and a $B_{(3)}$ ion it is clear that the crystalline electric field experienced by the centre is of axial symmetry. If the hole jumps from one of the four oxygen ions round the $B_{(4)}$ ion to another, the ESR absorption will remain anisotropic if the jumping frequency is low compared to detection frequency of the ESR equipment;

ad (5): the centre does not contain alkali or hydrogen ions.

The colour centres causing the four-*isotropic*-bands spectrum show the following features:

(1) they are also electron-hole centres $(g = 2.010)$;

(2) they dominate in the composition range where $x > 0.30$;

(3) they contain only one boron nucleus;

(4) the crystal field of the environment of the centre is of spherical symmetry (isotropic g-factor);

(5) they contain neither alkali nor hydrogen ions (g-factor independent of alkali ion).

In the composition range $0.30 < x < 0.50$ the relative number of boron ions in tetrahedral coordination N_4 varies between 0.38 and 0.28 and the mean number of non-bridging oxygen ions per polyhedron X increases from 0.09 to 0.72 (according to eqs (3.13) and (3.2)). Apart from the reactions mentioned above, it might be assumed that in this composition range a non-bridging oxygen ion would also produce a hole centre:

b-unit b_{II}-centre
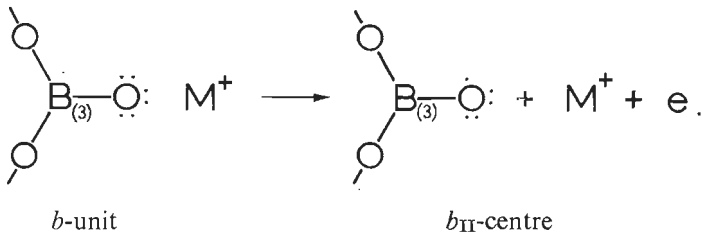
The b_{II}-centre meets all the requirements mentioned, except the one given under (4): it is *not* spherically symmetrical. It is therefore believed that the b_{II}-centre, if formed, does not cause the four isotropic ESR bands.

The c-centre contains four equivalent oxygen ions. A hole on one of them may jump to another oxygen ion and will find there an equally stable position. If this jumping of the hole occurs with a low frequency the ESR equipment will still "see" this centre as an axially symmetric one. This centre has been discussed previously and will be referred to further as a c_{III}-centre. If the hole jumps with a much higher frequency the ESR equipment is no longer able to distinguish between the four equal positions of the hole and will "see" the centre as spherically symmetrical. This model accounts for all the requirements mentioned above and will be referred to as a c_{II}-centre.

c_{III}-centre c_{II}-centre c_I-centre

anisotropic   isotropic   unresolved
quadruplet   quadruplet   hyperfine splitting
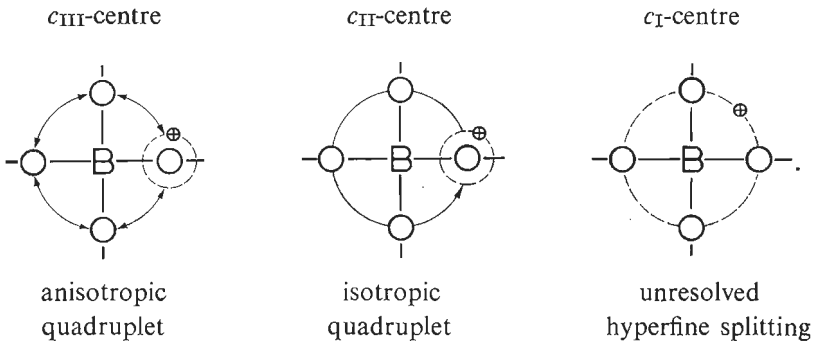
The broad band without hyperfine splitting ($g = 2.014$) observed in the rubidium- and caesium-borate glasses at high alkali-oxide concentrations ($x > 0.40$) and which was also found in lithium-borate glasses [9]) at far higher concentrations ($x > 0.60$) is believed to be due to a colour centre of type c_I consisting of an electron hole orbiting around a fourfold coordinated boron ion in the electron clouds of the surrounding oxygen ions. The hyperfine splitting is no longer resolved owing to the disintegration of the network and the large number of alkali ions in the environment of the centre at high alkali-oxide concentrations. This effect is also enhanced by an increase in the ionic radius of the alkali ions involved (cf. sec. 3.3.2.2).

We have thus succeeded in relating the main ESR and optical-absorption bands due to "alkali-independent" colour centres to a number of structural models. However, we have not yet discussed the minor band observed in both the ESR and the optical spectra of the alkali-borate glasses with $x < 0.30$. The optical band is found in all irradiated alkali-borate glasses with a low alkali-oxide concentration ($x < 0.15$) and in B_2O_3 glass (fig. 3.10) and is located at 2.4 eV. The ESR band is found at $g = 1.993$ (band 6 in table VII). Both locations are independent of the alkali ions. The absence of both bands above $x = 0.30$ and the fact that their energy is independent of the alkali ion suggests that they may arise from the same colour centre. The g-factor indicates that this colour centre is an electron centre. The centre does not exhibit a hyperfine structure, and its ESR band is relatively small. These experimental data are insufficient to allow the proposal of a structural model for this type of colour centres.

3.4. Conclusions

Three types of structural units may be distinguished in alkali-borate glasses (table VIII): a boron ion triangularly coordinated with three bridging oxygen ions (a-unit), a boron ion triangularly coordinated with two bridging ions and one non-bridging oxygen ion, with an adjacent alkali ion as a charge compensator (b-unit), and a boron ion tetrahedrally coordinated with four bridging oxygen ions, with an adjacent alkali ion as a charge compensator (c'-unit).

The amounts of each type of structural units depends on the concentration of the alkali oxide. A hypothesis for the structure of alkali-borate glasses has been proposed from which follow certain relations for the amounts of the various structural units (cf. sec. 3.2.5).

Upon irradiation, a number of colour centres are introduced into alkali-borate glasses which may be correlated with the structural units b and c'. No colour centre corresponding to the a-unit has yet been found.

During irradiation either the non-bridging oxygen ions in the b-unit may be moved to another site in the network (b_I-centre) or the alkali ion may be moved (b_{II}-centre). The former centre (b_I) is believed to cause the optical bands in the

TABLE VIII

Survey of types of structural units in alkali-borate glasses and the types of radiation-induced colour centres, with the corresponding optical- and ESR-absorption bands.

structural unit		induced absorption bands				type of colour centres formed upon irradiation		occurrence in borate glasses in order of decreasing number, at room temperature
		optical			ESR			
type	structure	type	energy (eV)		mean g-factor	type	model	
			298 °K	78°K				
a		—	—	—	—	—	—	—
b		b_I	1·5 1·75 1·95 2·4 ?	1·3 1·5 1·75 2·2 ?	—	b_I		(Cs) Rb K Na Li $x > 0.25$
		—	—	—	—	b_{II}		not found
c'		c_I	3·8		2·014 singlet	c_I		Cs Rb K Na Li large x
		c_{II}	~5		2·010 isotropic quadruplet $\Delta g = 0.008$	c_{II}		medium x
		c_{III}	>6		2·012 anisotropic quadruplet $\Delta g = 0.008$	c_{III}		Li Na K Rb Cs small x
—	?	—	2·4	—	1·993 singlet	—	?	small x

visible part of the spectrum, the energy as well as the band height of which depend on the alkali ion. A b_{II}-centre, which can be described as an electron hole captured on a non-bridging oxygen ion after the removal of the alkali ion from a b-unit, have not been found experimentally. Upon irradiation of a c'-unit, an electron may be removed from one of the four bridging oxygen ions. The excess of positive charge of the centre thus obtained is compensated by the removal of the adjacent alkali ion to another site in the network, the remaining centre consisting of a BO_4 group with an electron hole on one of the oxygen ions. The optical and ESR spectra of alkali-borate glasses provide evidence that these centres may occur in three different forms (c_I, c_{II} and c_{III}). The form to be found in a given glass depends on both the nature and the concentration of the alkali ions, although these do not actually form part of the c-centres.

In glasses with a high concentration of large alkali ions the c_I-centre will dominate. This centre may be described as an electron hole orbiting in the electron clouds of the four bridging oxygen ions of a BO_4 group. The interaction of the boron nucleus, which is visualized by the hyperfine splitting in the ESR spectrum, is not resolved owing to the desintegration of the network and the large number of alkali ions in the environment of the centre at high alkali-oxide concentrations. Hence a broad structureless band is found with a g-factor $= 2 \cdot 014$.

In glasses with a medium concentration of medium-sized alkali ions, such as potassium, the c_{II}-centres will dominate. These centres cause four hyperfine bands in the ESR spectrum, which are of the isotropic type, which means that the centres are of spherical symmetry. These centres are believed to consist of a BO_4 group with an electron hole captured on one of the oxygen ions, this hole jumping from one to another of the four oxygens with a high frequency so that the ESR equipment cannot "see" on which oxygen ion the electron hole is located. In these centres the interaction between the electron hole and the B^{11} nucleus is *not* influenced by the surroundings as described for the c_I-centres, so that the four hyperfine bands are observed in this case.

In glasses with a low concentration of small alkali ions, the c_{III}-centres will dominate. The hyperfine bands in the ESR spectrum now appear to be anisotropic, which means that the centres are of axial symmetry. This type of centre may be described as an electron hole captured on one of the four non-bridging oxygen ions in a BO_4 group. In this case the hole may also jump from one oxygen ion to another, however with a lower frequency than described for the c_{II}-centres, so that the ESR equipment now "sees" the electron hole on one of the oxygen ions of the BO_4 group. Apart from the centres b_I, c_I, c_{II} and c_{III}, a small band in the optical spectrum ($2 \cdot 4$ eV) and the ESR spectrum ($g = 1 \cdot 993$) suggests that at least one other type of colour centres is present in alkali-borate glasses with a low alkali-oxide content and in boric-oxide glass. The experimental evidence is insufficient to permit the suggestion for a model of these colour centres.

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4. COLOUR CENTRES IN ALKALINE-EARTH-BORATE GLASSES

4.1. Introduction

The study of the colour centres in binary alkaline-earth-borate glasses is limited by the small composition range in which homogeneous glasses can be formed (table IX [1])). However, on the addition of small amounts of alkali oxide the glass-forming range is extended to about 0-0.40 mol.MO (fig. 4.1). These pseudo-binary systems have also been included in this study of the radiation-

TABLE IX

Composition ranges where glasses are formed in the system x MO.$(1-x)$B$_2$O$_3$

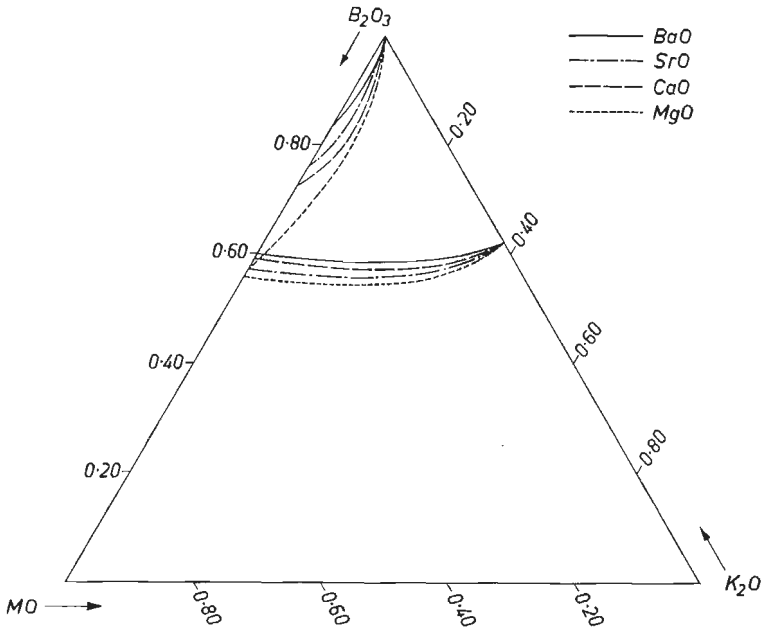| M	glass-forming range (values of x)
Ba	0·17-0·40
Sr	0·24-0·43
Ca	0·27-0·41
Mg	0·43-0·44

Fig. 4.1. Limits of the glass-forming range in the ternary system alkaline-earth oxide - potassium oxide - boric oxide [1]).

induced colour centres. No previous study of the radiation-induced colour centres in alkaline-earth-borate glasses is known to the author. In this section the colour centres in these glasses will be discussed in relation to the structure of the glass and with the insight into the colour centres in alkali-borate glasses obtained above.

4.2. The structure of alkaline-earth-borate glasses

4.2.1. *Introduction*

The quantities x, x_4, N_4, X, Y and Z, as defined for alkali-borate glasses, will also be used. The eqs (3.1) and (3.4) given in sec. 3.2.2 are also valid for the present glasses. It may be concluded from the phase separation occurring in alkaline-earth-borate melts in the composition range $0 < x < x_s$ (x_s equals the lower limit of glass formation (table IX)) that the alkaline-earth ions are taken up in the glass in a way differing from that for the alkali ions. This is clearly shown by the fact that the addition of a small amount of alkali oxide suppresses this phase separation. On the other hand it may be seen from the viscosity data of alkali- and alkaline-earth-borate glasses (the latter partially with addition of 3 mol. % K_2O) that the rigidity of the network has a maximum value at a composition comparable with x_{max} in the alkali-borate glasses[2,3,4]. In other words, the relative number of boron ions in fourfold coordination N_4 and the mean number of non-bridging oxygen ions per polyhedron X as a function of the composition x show a behaviour similar to that in the alkali-borate glasses. Recent NMR measurements on a series of calcium-borate glasses showed a maximum value of N_4 at $x = 0.40$ [5].

4.2.2. *A hypothesis for the structure of alkaline-earth-borate glasses*

It may be concluded from the NMR measurements mentioned above that the excess oxygen ions introduced by alkaline-earth oxide can give rise to the formation of BO_4 groups or non-bridging oxygen ions, as with the alkali-borate glasses. The ratio of the amounts of the two types of excess oxygen ions will depend on the composition and temperature. The structural units assumed to be present in an alkaline-earth-borate glass melt and the equilibria assumed between these units are shown in fig. 4.2. This scheme shows four competitive structural units containing an alkaline-earth ion. It is believed that a d-unit (non-bridging oxygen ion in a BO_4 group) is energetically unfavourable compared to the other structural units. In the alkali-borate glasses each alkali ion acts as charge compensator for one BO_4 group only, which enables the BO_4 groups to be located at any site of the network. This random location of the BO_4 groups (c'-unit in fig. 3.4) will be energetically favourable compared with a structure that requires the presence of double BO_4 tetrahedra (c''-unit in fig. 3.4). In alkaline-earth-borate glasses, however, each alkaline-earth ion must
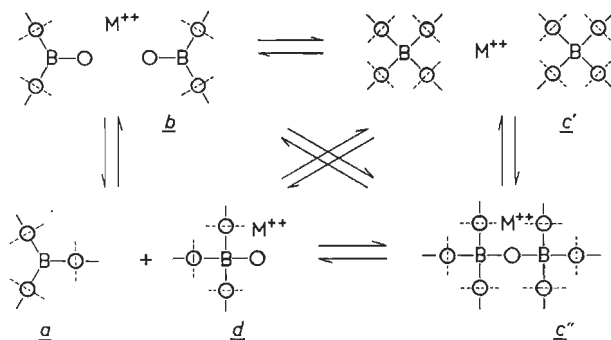
Fig. 4.2. Equilibria between the structural units present in a melt of an alkaline-earth-borate glass.

act as charge compensator for a pair of BO_4 groups, which requires the presence of double BO_4 tetrahedra. It may therefore be assumed that in the alkaline-earth-borate glasses the c''-unit is more stable than the c'-unit. The b-type units, where one alkaline-earth ion acts as charge compensator for two neighbouring non-bridging oxygen ions, are very likely to be formed in an alkaline-earth-borate glass.

These considerations lead to the supposition that the equilibrium between the b- and c''-units will determine the number of fourfold coordinated boron ions and the number of non-bridging oxygen ions in an alkaline-earth-borate glass. This supposition can be described by the following rules:

(1) each BO_4 tetrahedron is bound to one other BO_4 tetrahedron, in other words, double BO_4 tetrahedra are formed;

(2) non-bridging oxygen ions occur in BO_3 triangles only and are absent in BO_4 tetrahedra.

From these rules two limits for the relative number of boron ions in fourfold coordination, N_4, can be derived:

for $0 \leqslant x < \frac{1}{3}$: $x_4 = 1$; $N_4 = x/(1-x)$; $\quad X = 0$; $Y = 3 + x/(1-x)$;

for $x = \frac{1}{3}$ $\quad$: $x_4 = 1$; $N_4 = \frac{1}{2}$; $\quad\quad\quad\quad X = 0$; $Y = 3\frac{1}{2}$;

for $\frac{1}{3} < x < \frac{3}{4}$: $x_4 = \frac{1}{5}[3(1-x)/x-1]$; $\quad N_4 = \frac{1}{5}[3 - x/(1-x)]$; $\quad$ (4.1)
$\quad\quad\quad\quad\quad X = \frac{6}{5}[x/(1-x) - \frac{1}{2}]$; $\quad\quad Y = \frac{7}{5}[3 - x/(1-x)]$;

for $x = \frac{3}{4}$ $\quad$: $x_4 = 0$; $N_4 = 0$; $\quad\quad\quad\quad X = 3$; $Y = 0$.

As in the treatment in sec. 3.2.5 given for the alkali-borate glasses, the quantity N_4 may be represented by eq. (3.11):

$$N_4 = x_4 \, x/(1-x) = [x/(1-x)] \, [1 + \exp\{-(px+q)\}]^{-1}. \qquad (4.2)$$

A relation for N_4, which remains between the limits given by eq. (4.1) and which

shows a maximum at $x = 0.40$, is (fig. 4.3)

$$N_4 = [x/(1 - x)] \{1 + \exp (10.85x - 5.0)\}^{-1}. \qquad (4.3)$$

This relation does not provide an explanation for the phase separation occurring at low concentrations of alkaline-earth oxide (fig. 4.1). A possible explanation for this phase separation may be the following.

According to the equilibrium considerations of fig. 4.2 the incorporation of the alkaline-earth ion in an alkaline-earth-borate glass requires the presence of either two BO_4 groups bound to each other (structural unit c''), or two non-bridging oxygen ions close to one another (structural unit b). These structural units are, a priori, less probable than the single BO_4 group and the single BO_3 group with one non-bridging oxygen ion located in the glass network at random places. The a priori probability of pair formation, as represented by the structural units b and c'' (cf. fig. 4.2), increases with the number of single BO_4 groups and single BO_3 groups with a non-bridging oxygen ion, in other words, with an increase in the amount of metal oxide. From a thermodynamic point of view, the condition for pair formation may be characterized by a maximum in the thermodynamic potential ΔG in the composition range of $0 \leqslant x \leqslant x_s$. A ΔG-x curve of the shape of fig. 4.4 describes the phase separation occurring in the range $0 \leqslant x \leqslant x_s$. Each system with a composition in this range will tend to the lowest attainable ΔG. This means that a mixture of composition x_q will
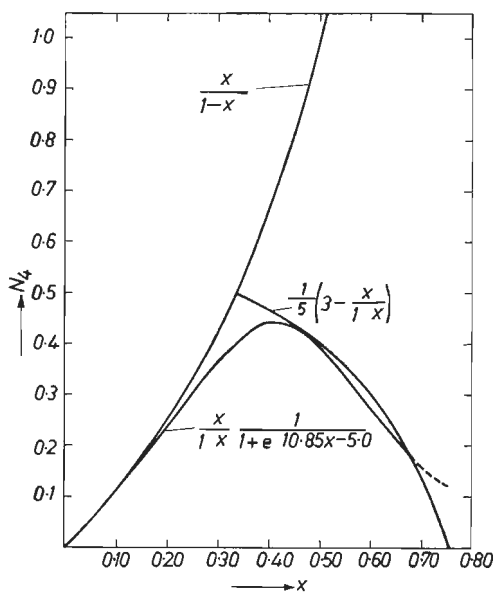
Fig. 4.3. The fraction of boron ions in tetrahedral coordination, N_4, as a function of the composition in alkaline-earth-borate glasses, according to eq. (4.3).
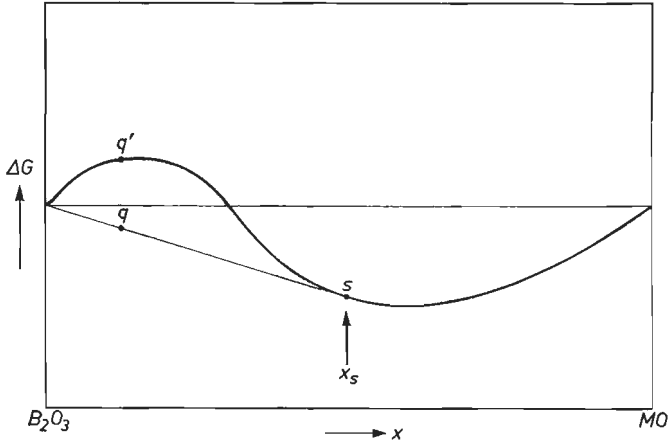
Fig. 4.4. The trend of the thermodynamic potential ΔG as a function of the composition x in the system alkaline-earth oxide – boric oxide.

lower its ΔG from q' to q by separation into two phases of composition $x = 0$ and $x = x_s$, in equilibrium. The equilibrium between the structural units b and c'' has no influence on this phase separation, as both types of units have in first approximation an equal a priori probability.

If a part of the BO_4 groups and the BO_3 groups with a non-bridging oxygen ion are not forced to form pairs, the ΔG of the system in the range $0 \leqslant x \leqslant x_s$ will be lowered. Hence, as the number of unpaired groups increases, the range in which phase separation occurs becomes narrower. Unpaired groups can be introduced in alkaline-earth-borate glasses by the addition of alkali oxide. It has been found that the addition of 3 to 6 mol. % K_2O to one mole of an alkaline-earth-borate glass can give homogeneous glasses without phase separation (fig. 4.1).

It can be seen from table IX that the value of x_s (fig. 4.4) is influenced by the nature of the alkaline-earth ion. A high ionic field strength $2z/a^2$ (cf. table X) gives rise to a high value of x_s.

4.3. Experimental results and discussion

4.3.1. *Introduction*

Generally speaking, the optical spectra of the alkaline-earth-borate glasses, given as plots of the optical density α (in cm^{-1}) versus the energy (in eV), show the same types of bands as the spectra of the alkali-borate glasses. There are however differences in the intensities of the bands as a function of the composition and the nature of the metal ion. It should also be remembered that most of the glasses contain a small amount of potassium oxide, which will certainly influence the shape of the various spectra. At appropriate compositions

in the series of barium- and strontium-borate glasses, comparative measurements have been made on samples with and without additional potassium oxide.

4.3.2. *The radiation-induced optical-absorption spectra*

Band b_I ($\approx$ 2 eV). The optical b_I-band, which is believed to arise from colour centres that may be described as a non-bridging oxygen-ion vacancy which has captured a pair of electrons, has been detected in glasses with a large amount of barium, strontium or calcium oxide (figs 4.8, 4.7, 4.6). In the composition range where magnesium-borate glasses could be prepared, no b_I-band was found (fig. 4.5). With a decrease in the ionic field strength (cf. table X) the b_I-band increases and shows a small shift to lower energy values. The trends described here for the alkaline-earth-borate glasses are similar to those observed with alkali-borate glasses, but appreciably weaker; this may be explained as follows. The formation of b_I-centres requires the presence of non-bridging oxygen ions in a network with a relatively low degree of coherence, in other words, a high alkaline-earth-oxide content and a low ionic field strength favour their formation. From the relation for N_4 for alkali- and alkaline-earth-borate glasses (cf. eqs (3.13) and (4.3)) it can be deduced that $X_{\text{alkaline earth}}$ is smaller for any value of x than X_{alkali} (cf. figs 3.7 and 4.3). All the alkaline-earth ions have a field strength exceeding the values for the alkali ions (table X), which means that the alkaline-earth ions with their partial network-forming character

Fig. 4.5. The radiation-induced optical spectra of magnesium-borate glasses.
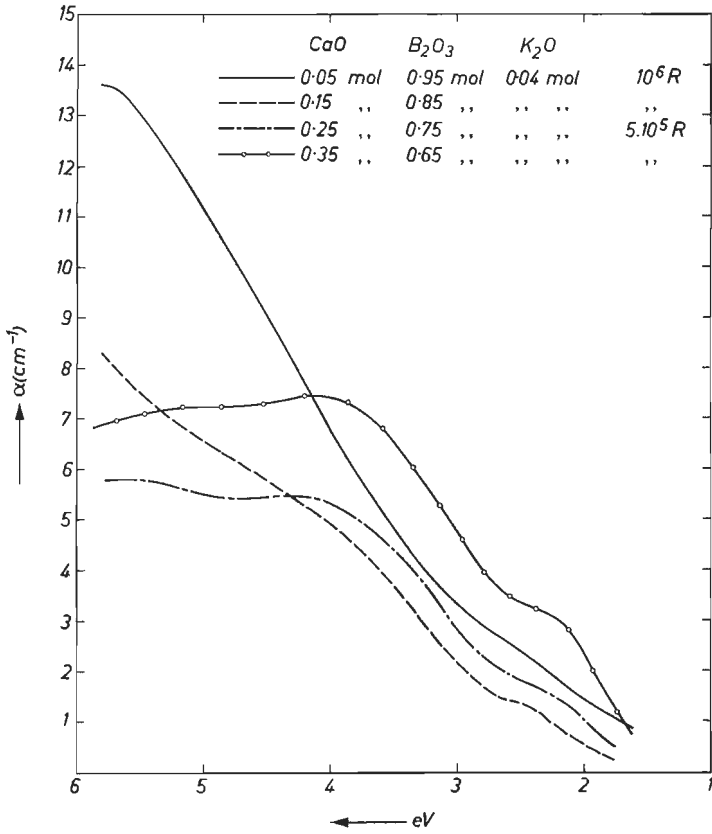
Fig. 4.6. The radiation-induced optical spectra of calcium-borate glasses.

TABLE X

Ionic field strength $2\,z/a^2$ of alkali and alkaline-earth ions

ion	$2z/a^2$	coord. number	ion	$2z/a^2$	coord. number
Li$^+$	0·45	4	Be^{2+}	1·51	4
Na$^+$	0·35	6	Mg^{2+}	1·02	4
K$^+$	0·27	9	Mg^{2+}	0·90	6
Rb$^+$	0·24	10	Ca^{2+}	0·69	8
Cs$^+$	0·21	12	Sr^{2+}	0·58	8
			Ba^{2+}	0·51	8

contribute to the coherence of the network to a greater extent than the alkali ions. The influence of the additional potassium oxide on the energy and the intensity of the band appears to be small (cf. fig. 4.8).

The bands c_I, c_{II} and c_{III} (3·9 eV, $\approx$ 5 eV, $>$ 6 eV, respectively). We concluded in the discussion of the spectra of the alkali-borate glasses, that it seems reasonable to assign the c_I-, c_{II}- and c_{III}-bands to colour centres which may be described generally as an electron hole captured in a BO_4 group (cf. sec. 3.3.4.3). These bands are discussed rather briefly here. The following trends may be observed (figs 4.5, 4.6, 4.7, 4.8):

— an increase in the alkaline-earth-oxide content (x) generally causes the c_{III}-band to decrease in comparison with the c_{II}- and c_I-bands;
— with a further increase in x the c_{II}-band decreases in comparison with the c_I-band;
— both effects increase with a decrease in the ionic field strength.

Fig. 4.7. The radiation-induced optical spectra of strontium-borate glasses.
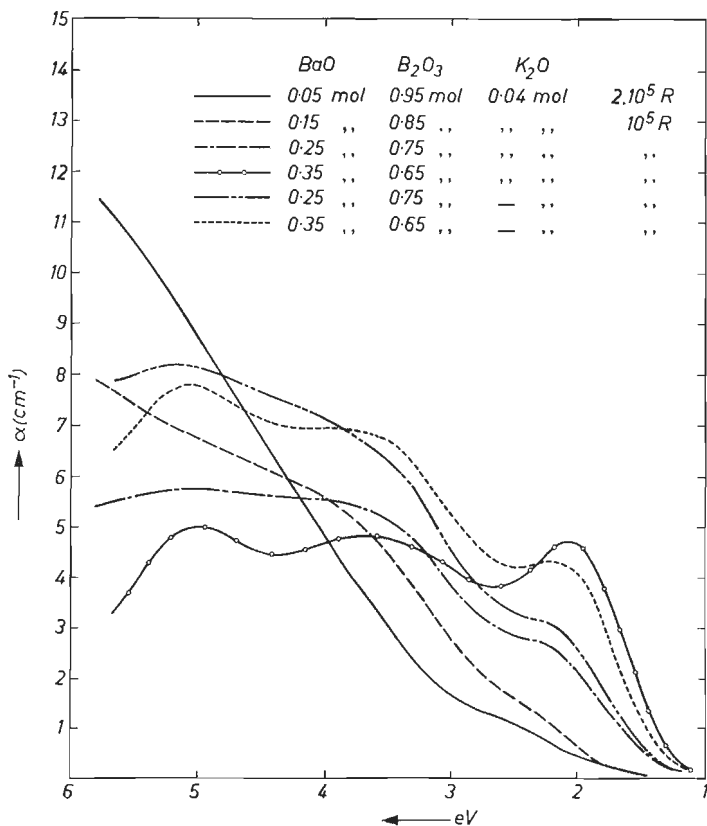
Fig. 4.8. The radiation-induced optical spectra of barium-borate glasses.

These trends agree reasonably with the changes in the intensity of the c_I-, c_{II}- and c_{III}-band in the alkali-borate glasses, which would seem to indicate a similarity between the structural changes in the alkali- and the alkaline-earth-borate glasses as a function of the composition and the field strength.

Another indication of this similarity may be found in the ratio of the un-resolved c_I-band heights (a) at room temperature (298 °K) and liquid-nitrogen temperature (78 °K) as a function of the composition. The values of the ratio a_{298}/a_{78} for the various alkaline-earth ions in borate glasses are all of the same order of magnitude (table XI), values for the barium-borate glasses being on the low side. These values are also of the same order of magnitude as found for the alkali-borate glasses (cf. sec. 3.3.2.2).

TABLE XI

The ratios α_{298}/α_{78} of the c_I-band (3·8 eV) in alkaline-earth-borate glasses with (K^+) and without (—) additional potassium oxide

ion x	0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40
$Mg^{++}(K^+)$	—	—	—	(0·37)	0·29	0·23	0·27	0·28
Ca^{++} (K^+)	—	—	0·25	0·25	0·27	0·27	0·27	—
Sr^{++} (K^+)	—	—	0·25	0·27	0·22	0·26	0·25	—
Sr^{++} (—)	—	—	—	—	—	0·30	0·32	—
Ba^{++} (K^+)	—	—	0·23	0·19	0·14	0·10	0·10	—
Ba^{++} (—)	—	—	—	0·19	0·19	0·18	0·18	—

4.3.3. *The radiation-induced ESR spectra*

The ESR spectra of irradiated alkaline-earth-borate glasses show the same types of bands as the alkali-borate-glass spectra, but differences are found in the composition dependence of the bands.

In glasses with a small x, the six bands of the B_2O_3-glass spectrum are found. As we have seen, these arise (apart from the small band at $g = 1\cdot993$) from colour centres with a structure which may be described as an electron hole captured on one oxygen ion in a BO_4 group. The hole may jump to another of the four oxygen ions with a low frequency, so that the ESR equipment "sees" the hole on one particular oxygen ion (c_{III}-centre, sec. 3.3.4.3). This is the anisotropic four-band spectrum. With an increase in x this spectrum gradually changes into an isotropic four-band spectrum which may be assigned to an electron-hole centre, the hole being captured on one of the four surrounding oxygen ions of a BO_4 group. In this case the hole jumps from one of the four oxygen ions to another with a high frequency so that the ESR equipment cannot "see" on which oxygen the hole is located (centre type c_{II}). An almost pure isotropic four-band spectrum is found in the potassium-borate glass with $x = 0\cdot35$ (fig. 3.22).

In the series of magnesium-borate glasses (fig. 4.9) the replacement of the anisotropic by the isotropic four-band spectrum is not yet accomplished even at $x = 0\cdot40$. At this composition the spectrum still resembles the complex intermediate spectrum found for the potassium-borate glass with $x = 0\cdot30$ (fig. 3.22). In the series of calcium-, strontium- and barium-borate glasses (figs 4.10, 4.11, 4.12) the four isotropic bands are well established in systems with $x = 0\cdot35$. The resolution of these spectra becomes however less pronounced in the sequence calcium, strontium and barium. This effect is similar to the decreased resolution of the four bands in the rubidium-borate glasses
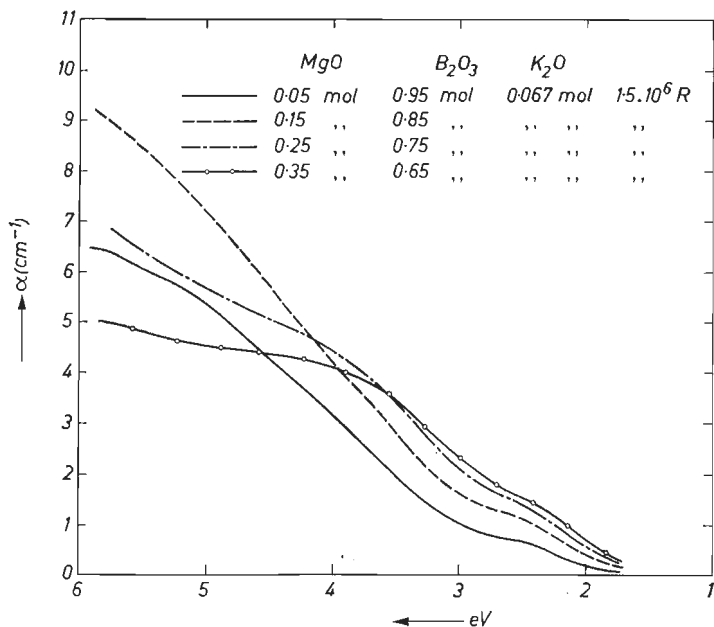
Fig. 4.9. The radiation-induced ESR spectra of magnesium-borate glasses.

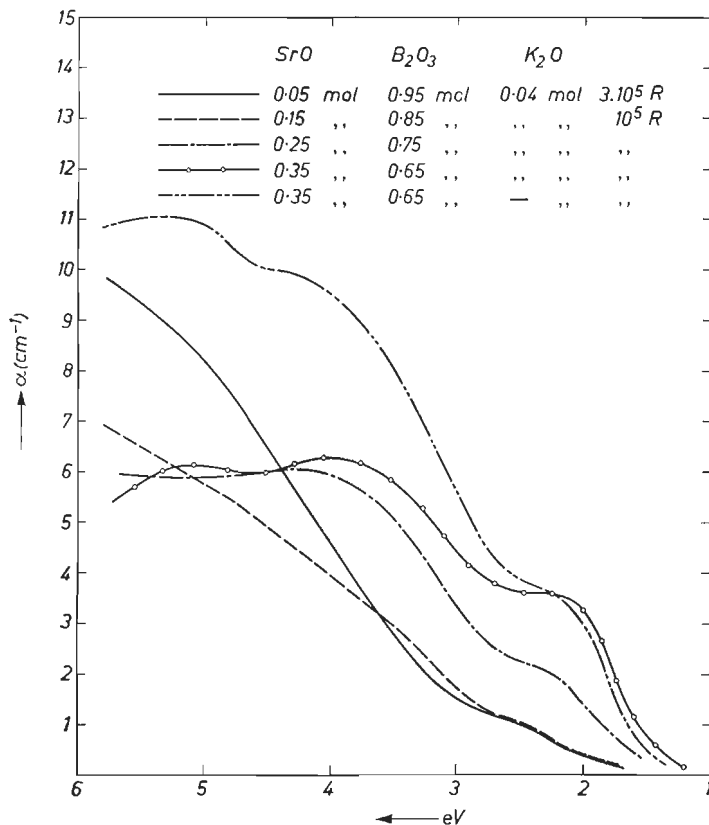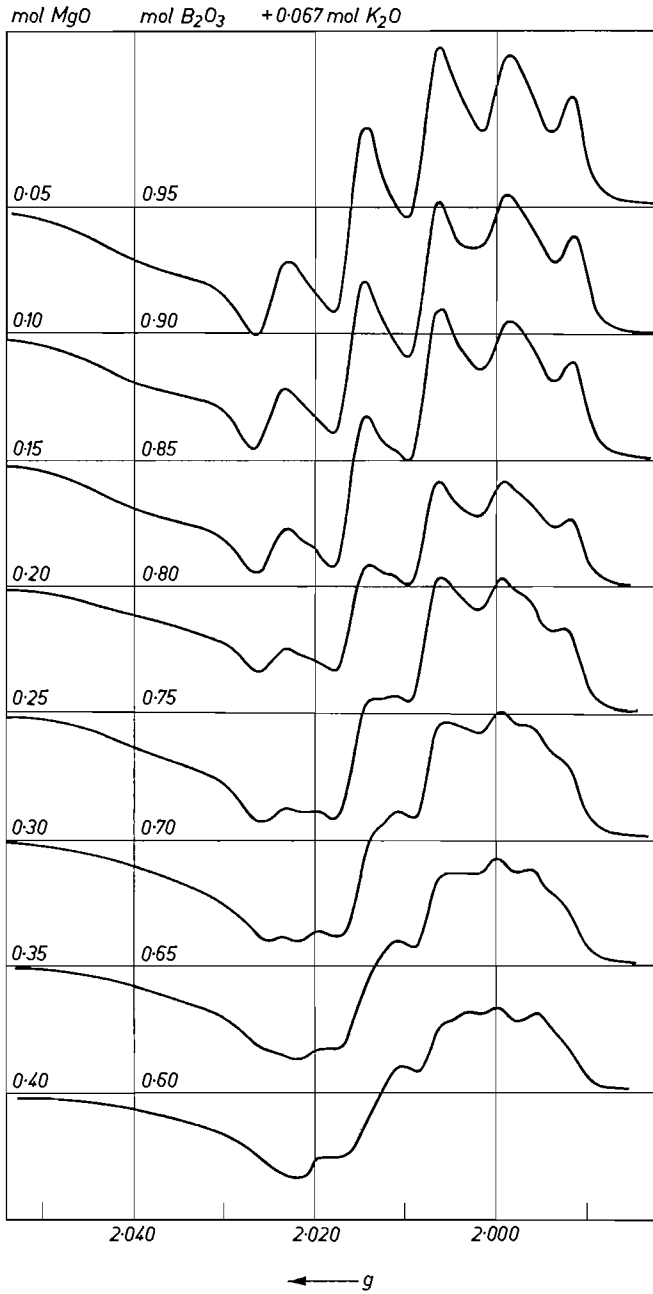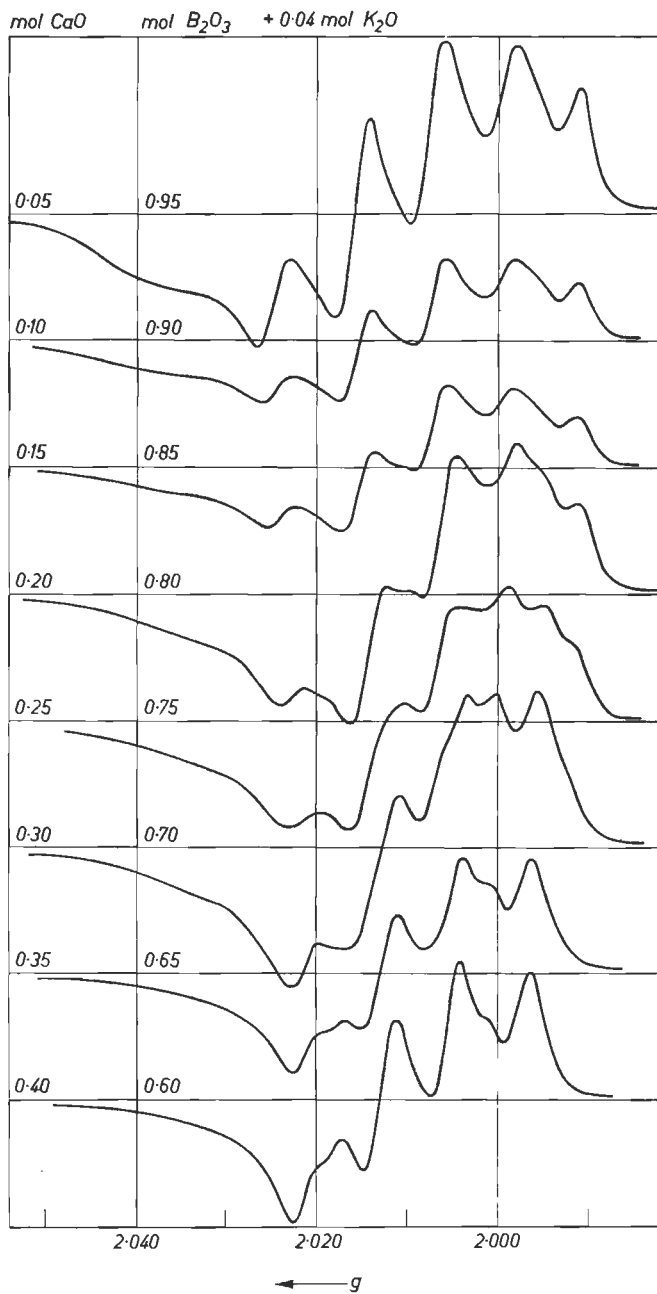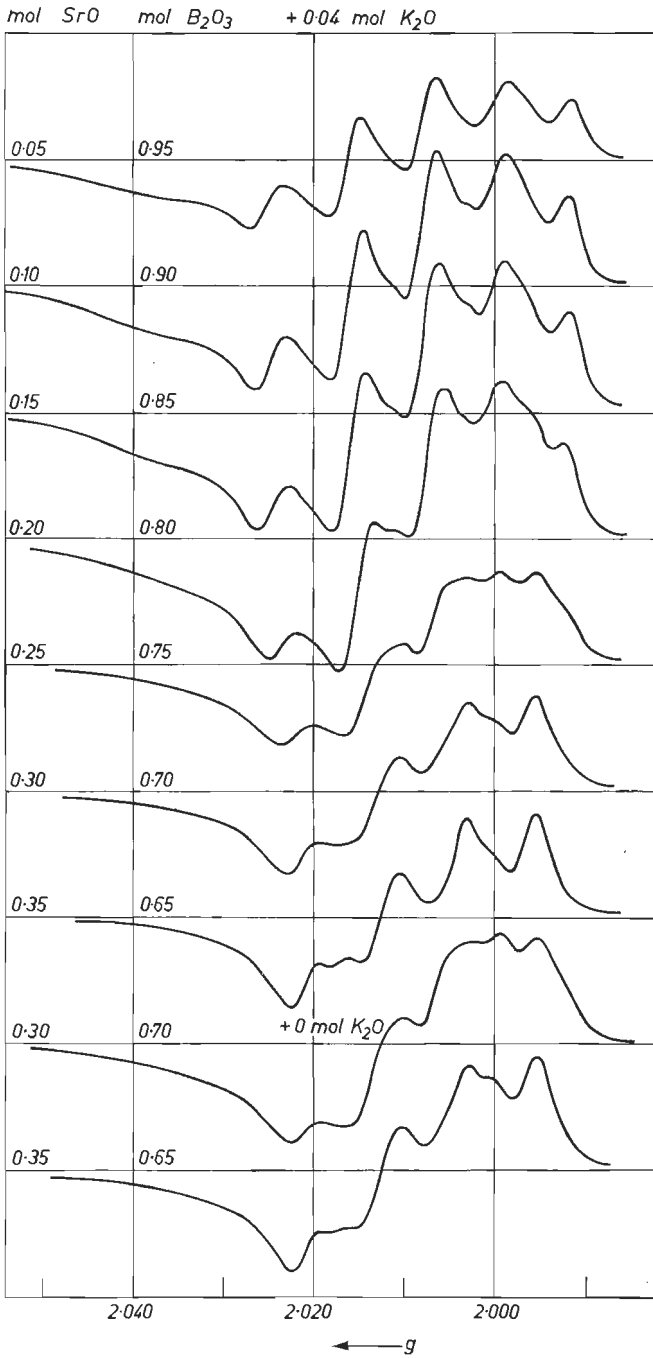Fig. 4.10. The radiation-induced ESR spectra of calcium-borate glasses.

Fig. 4.11. The radiation-induced ESR spectra of strontium-borate glasses.
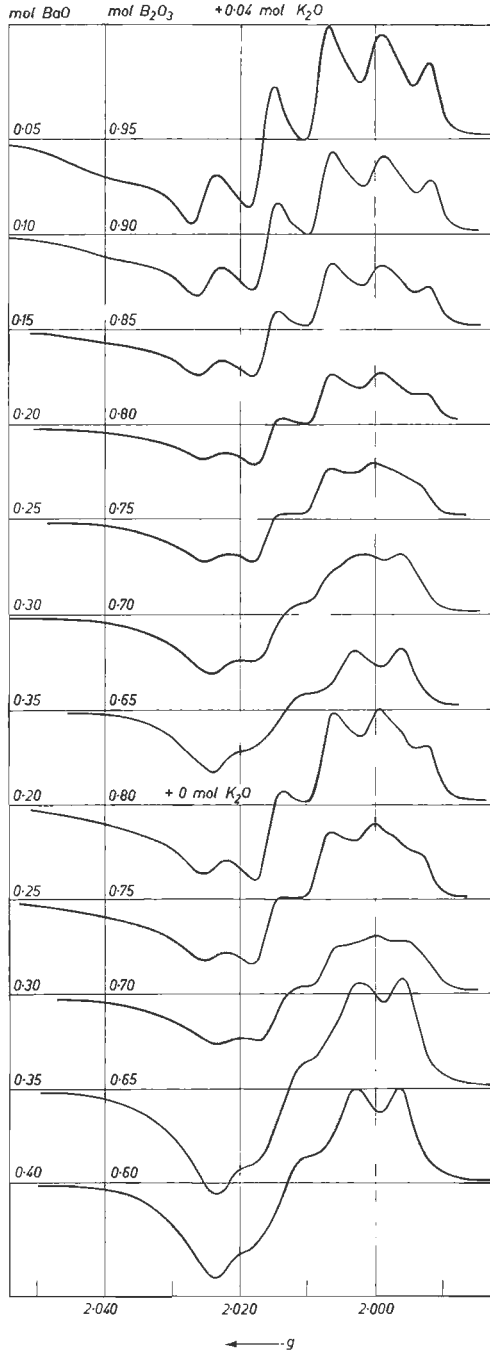
Fig. 4.12. The radiation-induced ESR spectra of barium-borate glasses.

and their complete disappearance in a caesium-borate glass of composition $x = 0\cdot40$. The remaining single band in the caesium-borate-glass spectrum has been attributed to an electron-hole centre, the hole orbiting in the electron clouds of the oxygen ions in a BO_4 group (c_I-centre), but the centre being influenced to such an extent by the desintegration of the network that a resolved hyperfine structure could not be observed. Such an unresolved broad band is also believed to be present as background in many other glasses, but is only clearly observable in the strontium- and barium-borate glasses with a high value of x.

From a number of spectra of barium-borate glasses with and without additional potassium oxide it may be concluded that the local structure (the structural units) is only slightly influenced by the potassium ions. However, the bulk structure does definitely change on the addition of potassium oxide, as may be seen from the vanishing of the phase separation.

4.4. Conclusions

In an alkaline-earth-borate glass three types of structural units may be distinguished (table XII): a boron ion triangularly coordinated by three bridging oxygen ions (a-unit), two boron ions both triangularly coordinated by two bridging oxygen ions and one non-bridging oxygen ion with an alkaline-earth ion as a charge compensator (b-unit), and two adjacent boron ions both tetrahedrally coordinated by four bridging oxygen ions with an adjacent alkaline-earth ion as a charge compensator (c''-unit). The amounts of each type of structural units depend on the concentration of the alkaline-earth oxide. From a hypothesis for the structure of alkaline-earth-borate glasses relations have been derived for the relative number of boron ions in tetrahedral coordination (N_4) and the mean number of non-bridging oxygen ions per polyhedron (X).

Upon irradiation colour centres are formed of the types b_I, c_I, c_{II} and c_{III}, as are found in alkali-borate glasses. The dependence on the concentration and the type of alkaline-earth ions of the numbers of the various types of centres differs from the dependence, found in the alkali-borate glasses. A number of marked differences are:
(1) the number of b_I-centres is considerably smaller;
(2) the energy of the b_I-band is less influenced by a decrease of the field strength of the alkaline-earth ions;
(3) the decrease in the number of c_{III}-centres combined with an increase in the number of c_I-centres with a rise of the alkaline-earth-oxide concentration is less pronounced.

These effects may be explained as follows. The value of N_4 for *alkaline-earth*-borate glasses is greater and hence the value of X is smaller for any given x-value than for the *alkali*-borate glasses. Furthermore, the alkaline-earth ions

TABLE XII

Survey of types of structural units in alkaline-earth borate glasses and the types of radiation-induced colour centres, with the corresponding optical- and ESR-absorption bands

structural unit		induced absorption bands			type of colour centres formed upon irradiation		occurrence in borate glasses in order of decreasing number
		optical		ESR			
type	structure	type	energy (eV)	mean g-factor	type	model	
a	(structure diagram)	—	—	—	—	—	—
b	(structure diagram, M^{++})	b_I	2·1 2·1 2·2 2·3	—	b_I	(model diagram, B M)	Ba Sr Ca Mg — $x > 0.25$
c''	(structure diagram, M^{++})	c_I	3·8	2·014 singlet	c_I	(model diagram)	Ba Sr Ca Mg — large x
		c_{II}	~5	2·010 isotropic quadruplet $\Delta g = 0.008$	c_{II}	(model diagram)	medium x
		c_{III}	>6	2·012 anisotropic quadruplet $\Delta g = 0.008$	c_{III}	(model diagram)	Mg Ca Sr Ba — small x
—	—	—	2·4	1·993 singlet	—	?	small x

have a higher field strength. Thus the degree of coherence of the network of alkaline-earth-borate glasses is usually higher. Therefore:

ad (1): a smaller value of X and a higher degree of coherence make the formation of b_I-centres less likely;

ad (2): the small change in the b_I-band energy is also believed to be due to the higher degree of coherence;

ad (3): the formation of c_I-centres is favoured by the presence of large ion and a high alkaline-earth-oxide concentration; the relatively small ionic radii of the alkaline-earth ions may explain the less pronounced effect here.

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5. COLOUR CENTRES IN PHOSPHATE GLASSES

5.1. Introduction

Kreidl and Hensler [1,2] were the first to report on colour centres in phosphorus-containing glasses, in their studies on gamma-irradiated multicomponent glasses. They studied the influence on the formation of colour centres of minor amounts of added impuritites, such as Ce, Ti, Fe, etc.

Bishay [3] studied the influence of the various alkali and alkaline-earth ions on the induced optical-absorption bands in a number of irradiated phosphate glasses. Small additions of Ge, Ti, Fe, Tl, Nb and As were found to inhibit the induced colouration in the visible part of the optical spectrum.

Karapetyan and Yudin [4] were the first to propose models, based on their ESR and optical experiments with sodium-, calcium- and zinc-phosphate glasses, to explain the reaction products of the ionizing radiation in phosphate glasses.

Tucker [5] explained his ESR data with a structural model for the colour centres in phosphate glasses which differs essentially from Karapetyan and Yudin's model.

Bishay and Ferguson [6] have reported on the influence of the polarizing power, the coordination number of network-forming and -modifying ions, the concentration of non-bridging oxygen ions and the presence of multivalent network-forming or -modifying ions on the induced colouration in phosphate glasses.

In a recent paper, Schreurs and Tucker [7] established an empirical correlation between the ESR spectra and the optical spectra of irradiated sodium-silicate glass and calcium-metaphosphate glass. They proposed a model for one of the colour centres produced in these glasses, which gives rise to optical absorption in the visible region of the spectrum and a characteristic ESR absorption, which they believed to be applicable to a wider variety of glasses.

In this chapter a systematic study of optical and ESR spectra of irradiated, simple binary phosphate glasses will be given. The results and conclusions will be compared with those of the authors mentioned above.

5.2. The structure of phosphate glasses

5.2.1. *Introduction*

The structure of phosphate glasses has been shown to be similar to that of silicate glasses [8]. Each phosphorus ion is tetrahedrally surrounded by four oxygen ions and each pair of PO_4 tetrahedra may only share one oxygen ion with one another. However, the pentavalency of the phosphorus ion gives rise to anomalies in the properties of phosphate glasses as compared with corre-

sponding silicate glasses. In the following sections the evolution of the theory of the structure of phosphate glasses will be reviewed and discussed.

5.2.2. *The structure according to Kordes et al.*

Kordes, Vogel and Feterowski [9]) studied the influence of the composition of various binary phosphate glasses on the molecular volume, the refractive index n_D, the Abbe number v, the density and the molar refraction. They concluded that phosphate glasses which show a gradual change in these physical quantities with the composition, must be isostructural with the corresponding silicate glasses. These are therefore called the *normal phosphate glasses*. On the other hand, Kordes et al. observed abrupt changes in the physical properties of certain phosphate glasses at the metaphosphate composition. These *phosphate glasses* are called *anomalous*. Kordes explains the difference in behaviour as follows: P_2O_5 glass itselfs consists of an extended network of PO_4 tetrahedra, each of which shares its three corners with other tetrahedra, whilst the unshared oxygen ion is doubly bonded to the phosphorus ion. In the "normal" glasses addition of the metal oxide results in a breakage of P-O-P bonds, giving non-bridging singly bonded oxygen ions, the metal ions entering into the interstices of the network as modifiers. In the "anomalous" phosphate glasses, such as those containing BeO, MgO or ZnO, the metal ions are four-fold coordinated and act as network formers in the range from pure P_2O_5 to the metaphosphate composition. In the range beyond the metaphosphate composition the extra metal ions act as modifiers, entering into the interstices of the network, as in the normal phosphate glasses. According to Kordes this change in behaviour of the metal ions at the metaphosphate composition may be used to explain the abrupt changes in the property-composition curves. From this theory one may conclude that in the case of the normal phosphate glasses the coherence of the network decreases with increasing amount of metal oxide. In the case of the anomalous phosphate glasses the coherence of the network increases up to the metaphosphate composition. Beyond this composition the coherence decreases with increasing amount of metal oxide.

5.2.3. *The structure according to Elyard et al.*

Elyard, Baynton and Rawson [10]) investigated the influence of the composition of phosphate glasses on the thermal-expansion coefficient and the activation energy for viscous flow. Their data show a decrease in the expansion coefficient and an increase in the activation energy of viscous flow with increasing metal-oxide content in the composition range between pure P_2O_5 and the metaphosphate glass for both normal and anomalous phosphate glasses. In other words, an increase in the metal-oxide content in this composition range in both types of phosphate glasses gives rise to an increase in the rigidity of the glass network. They put forward two explanations for this effect:

(1) Certain groups of polymerised PO_4 tetrahedra may exist in a pure P_2O_5 glass (fig. 5.1a). On addition of metal oxide, a P-O-P bond is opened in two neighbouring groups and -O-M-O-bridges are formed between these two groups (fig. 5.1b). This mechanism requires bivalent metal ions and cyclic
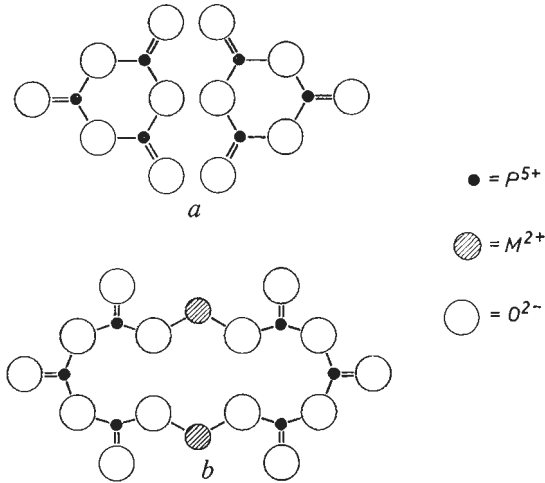
Fig. 5.1. Structure of a phosphate glass, according to Elyard et al. [10].
(a) Structure before addition of MO.
(b) Structure after addition of MO.

polymers of PO_4 tetrahedra. The oxygen ions doubly bonded to a phosphorus ion are not involved in this mechanism, hence their number remains unchanged after addition of metal oxide.

(2) Addition of metal oxide to a pure P_2O_5 glass causes breakage of P-O-P bonds, leading to the presence of singly bonded non-bridging oxygen ions with an adjacent metal ion as a charge compensator. If this metal ion is also located near a doubly bonded non-bridging oxygen ion, there will be a tendency for valancy electrons to move from the latter to a second singly bonded non-bridging oxygen ion, enabling a second -O-M-O-bridge to be formed:
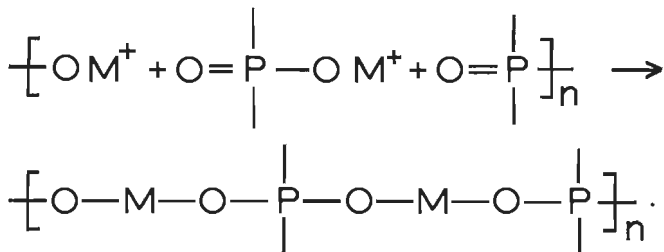
This mechanism is operative with both monovalent and bivalent metal ions and explains the decrease in the number of doubly bonded non-bridging oxygen ions on addition of metal oxide.

Both explanations ascribe a certain network-forming action to the metal ions.

5.2.4. *The structure of alkali-phosphate glasses* [11]

Kordes et al. and Elyard et al. did not discuss the structure of alkali-phosphate glasses. This subject will therefore be discussed separately in this section.

Alkali-phosphate glasses dissolve easily in water. It was found that groups of polymerised PO_4 tetrahedra present in the glasses are practically unaffected by hydrolysis in aqueous solution at room temperature [12]. This has led to a number of paper-chromatographic investigations on the constitution of the groups of polymerised PO_4 tetrahedra by Westman and his co-workers [11,13,14, 15].

It was established that linear PO_4 polymers exist at each composition with more alkali oxide than the metaphosphate composition, the chain lengths being distributed around a certain mean value. At lower alkali-oxide contents, i.e. below the metaphosphate composition, the phosphate glasses have a normal three-dimensional network. This confirmed the picture of the structure of phosphate glasses previously postulated by Van Wazer [16] on the basis of concepts developed from studies of linear organic polymers. Brady [17] and Milberg and Daly [18,19] concluded from their X-ray experiments that sodium-metaphosphate glass consists of infinite linear polymers of PO_4 tetrahedra cross-linked by O-Na-O bridges. In addition it may be concluded that in this glass the sodium ions still act — although relatively weakly — as network-forming ions to give the necessary bonding forces between the linear PO_4-polymer chains.

5.2.5. *Some critical remarks*

The division of the phosphate glasses into two groups, normal and anomalous, as proposed by Kordes et al., was based on the Zachariasen network theory in its simplest form [20,21]. Elyard et al. pointed out that the properties of phosphate glasses must be explained by a somewhat modified Zachariasen theory. Modifications are necessary to account for the gradual increase in the rigidity of the network, indicated by the decrease in expansion coefficient and the increase in the activation energy for viscous flow, as the metal-oxide content of the glasses is increased.

Kordes suggested that the breaks in the property-composition curves of his anomalous phosphate glasses (magnesium- and zinc-phosphate glasses) may be due to the fact that beyond the metaphosphate composition the extra metal ions no longer act as fourfold-coordinated network formers, which strengthen the network, but as network modifiers with a higher coordination number,

which strengthen the network to a lesser extent. This hypothesis does not hold for certain properties of barium-, strontium- and calcium-phosphate glasses which show extreme values at the metaphosphate composition (see e.g. ref. 9, fig. 6).

Elyard et al. pointed out that beyond the metaphosphate composition a difference still exists between the magnesium-, zinc-, cadmium- and lead-phosphate glasses and the barium-, strontium- and calcium-phosphate glasses as regards the network-modifying and network-forming character of these ions. The division into two groups was based on the fact that phosphate glasses with ions of the first group can be formed up to the pyrophosphate composition ($2M^{II}O \cdot P_2O_5$). With ions of the second group, devitrification already occurs when about 7 mol.% $M^{II}O$ is added beyond the metaphosphate composition. These remarks do not appear to support Kordes' views, but on the other hand they do not explain the extreme values at the metaphosphate composition either.

5.2.6. *A hypothesis for the structure of binary phosphate glasses*

Generally speaking, the rigidity of a glass network depends on the number of bridging oxygen ions per polyhedron. In the case of phosphate glasses we have a more complex structure as compared to that of the silicate glasses.

A hypothesis for the structure of phosphate glasses must account for the following effects:
(1) the increasing rigidity with increasing amounts of metal oxide;
(2) the differing increase in rigidity for each metal oxide added;
(3) the marked change in many properties at the metaphosphate composition.

According to Elyard's first structural model (cf. sec. 5.2.3) the network is strengthened only by the presence of cyclic polymers of PO_4 tetrahedra and bivalent metal ions. However, a chromatographic analysis of a sodium-metaphosphate glass shows [14] that 92·5% by weight of the polymers are non-cyclic. Moreover, the presence of P-O-Na-O-P cross-links in this glass has been established by X-ray analysis [17,18,19]. It may therefore be assumed that strengthening according to Elyard's first model gives only a small contribution to the rigidity of the phosphate-glass network (see point (1)).

Elyard's second model, which allows bridges between singly and doubly bonded non-bridging oxygen ions by means of a metal ion, does not require any special conditions such as the presence of cyclic polymers and bivalent metal ions, as his first model did. Any metal ion may form these bridges, producing an increased rigidity of the network. However, the strength of these bridges depends on the metal ion used, since the network-forming action of the metal ion will differ from ion to ion.

The order of magnitude of this network-forming action may be represented by the field strength [22] $2 \, z/a^2$, where 2 and z are the charges on the oxygen ion and the cation, respectively, and a is the distance in Å between the ionic centres

of the oxygen ion and cation. Network formers are found among the high-field-strength ions (table XIII).

## TABLE XIII

Ionic field strength $2\, z/a^2$ of a number of ions

ion	coord. number	$2z/a^2$	ion	coord. number	$2z/a^2$	ion	coord. number	$2z/a^2$
P^{5+}	4	4·33	Ti^{4+}	6	2·08	Ca^{2+}	8	0·69
B^{3+}	3	3·22	Al^{3+}	4	1·94	Pb^{2+}	6	0·68
As^{5+}	4	3·20	Al^{3+}	6	1·69	Sr^{2+}	8	0·58
Si^{4+}	4	3·14	Zr^{4+}	8	1·55	Ba^{2+}	8	0·51
V^{5+}	4	3·08	Be^{2+}	4	1·51	Li^{+}	4	0·45
B^{3+}	4	2·90	Th^{4+}	8	1·28	Na^{+}	6	0·35
Ge^{4+}	4	2·65	Zn^{2+}	4	1·08	K^{+}	9	0·27
Sb^{5+}	4	2·45	Mg^{2+}	4	1·02	Rb^{+}	10	0·24
			Mg^{2+}	6	0·90	Cs^{+}	12	0·21

Elyard's second model combined with the influence of the field strength of the metal ions may account for the effects mentioned under (1) and (2). It is unlikely that the effect mentioned under (3) can be explained by a sudden change in coordination number of the metal ions at the metaphosphate composition (cf. Kordes' model), as observed in phosphate glasses containing metal ions with an appreciable difference in field strength.

Van Wazer [16]) postulated that the introduction of metal ions in a phosphate glass may break the network at the weak places in the PO_4 polymers, i.e. at places where the polymers branch. It has been concluded [11]) from this theory that a metaphosphate glass consists of infinitely long PO_4 chains cross-linked by O-M-O bridges, as described by Elyard's second model. A further addition of metal oxide gives rise to a decrease in chain length. It is believed that below the metaphosphate composition the phosphate glasses have a three-dimensional network structure. Above this composition they consist of finite, linear polymer chains of PO_4 tetrahedra. This structural change at the metaphosphate composition is believed to be responsible for the effect mentioned under (3).
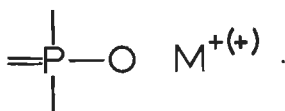
It follows from the proposed structure of phosphate glasses that four different types of structural units are involved.

(I)   An oxygen ion bound between two phosphorus ions:

$$\equiv\!\!\overset{\displaystyle |}{\underset{\displaystyle |}{P}}\!-\!O\!-\!\overset{\displaystyle |}{\underset{\displaystyle |}{P}}\!\!\equiv \ .$$
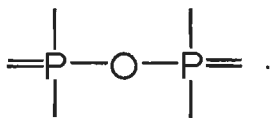
This unit contains a *classical bridging oxygen ion*.

(II)   An oxygen ion bound to one phosphorus ion with one valency only:

$$\equiv\!\!\overset{\displaystyle |}{\underset{\displaystyle |}{P}}\!-\!O \quad M^{+(+)} \ .$$

The negative charge of the oxygen ion (a *classical non-bridging oxygen ion*) is compensated by a metal ion M^+ acting as a network modifier.

(III) An oxygen ion bound between a phosphorus and a metal ion, the latter acting as a network former:

$$-\!\overset{\displaystyle |}{\underset{\displaystyle |}{P}}\!-\!O\!-\!\overset{\displaystyle |}{\underset{\displaystyle |}{M}}\!- \ .$$
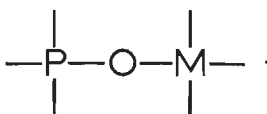
This oxygen ion may also be classified as a *bridging oxygen ion*. It is clear that the contribution to the rigidity of the network of this type of oxygen is smaller than that of the classical bridging oxygen ion.

(IV) An oxygen ion doubly bonded to one phosphorus ion:

$$-\!\overset{\displaystyle |}{\underset{\displaystyle |}{P}}\!=\!O \ .$$
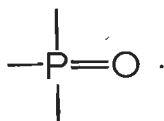
This oxygen ion does not contribute to the rigidity of the network and is therefore in this respect akin to the classical *non-bridging oxygen ion*.

In theory a metal ion in a phosphate glass may be bound purely ionically to the network by an oxygen ion of unit II or purely covalently by oxygen ions of unit III. In a real phosphate glass, however, the metal ions are believed to be bound to the glass network in an intermediate way, which may be represented as a *hybrid* between the structural units II and III. A low field strength of the metal

ions involved gives the hybrid a type-II character, whereas a high field strength causes the hybrid to adopt a type-III character:

$$=\overset{|}{\underset{|}{P}}-O \quad M^{+(+)} \quad \rightleftharpoons \boxed{HYBRID} \rightleftharpoons \quad -\overset{|}{\underset{|}{P}}-O-\overset{|}{\underset{|}{M}}- \; .$$

unit II   unit III
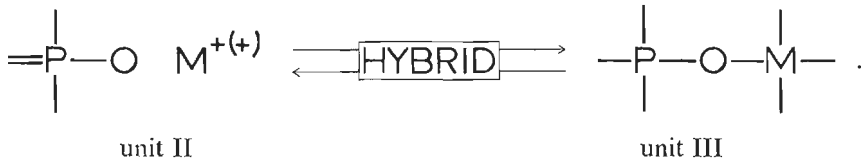
Pure P_2O_5 glass contains the units I and IV only. Addition of metal oxide in fact gives rise to the formation of a hybrid between the units II and III at the expense of a part of the units IV (cf. sec. 5.2.3).

It will be noticed that these structural units are considered as being centred on the oxygen ion, since the nature of this ion is the most important feature of these units; the structural units of the borate glasses, on the other hand, were represented as centred on the boron ion, since here the coordination number of the boron is the important feature.

5.3. Experimental results and discussion

5.3.1. *Introduction*

The same conventions are used for a quantitative discussion of the ESR and optical spectra as in earlier sections (cf. secs 1.3.2, 2.2 and 2.3.2).

The compositions of the phosphate glasses to be discussed are given in mole fractions of metal oxide (M_2O or MO) and fractions of half a mole of phosphorus pentoxide ($PO_{2.5}$). These compositions are directly comparable with those of silicate glasses, which are given in mole fractions of metal oxide and SiO_2.

5.3.2. *The radiation-induced optical-absorption spectra*

5.3.2.1. The bands in the spectra

Three major bands may be observed in the radiation-induced optical-absorption spectra of phosphate glasses, which are given as plots of the optical density α (in cm^{-1}) versus the energy (in eV)(fig. 5.2).

The energy of the 2·4-eV band (band II) is practically independent of the metal ion, while that of the 3-eV band (band III) changes with the metal ions. At a higher energy (about 6 eV) a band (band IV) is found which could not be observed directly because of the high intrinsic absorption of the phosphate glasses in this region. However, the incline of the absorption curve between 4 and 5 eV gives an indication of the magnitude of this band. The absence of a band I will be explained below.
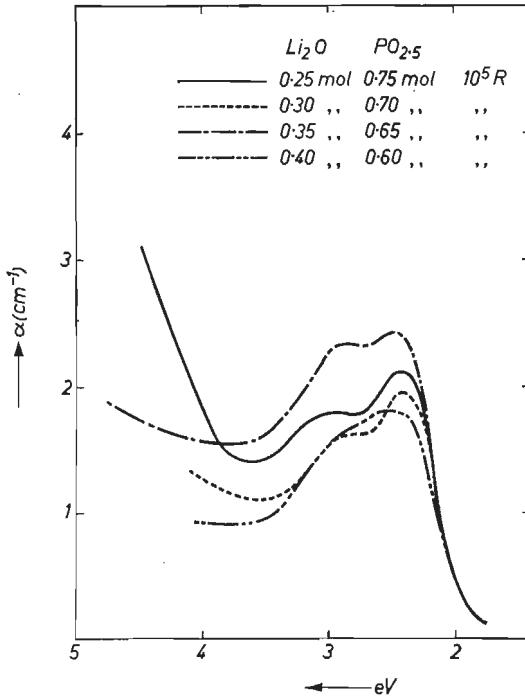
Fig. 5.2. The radiation-induced optical spectra of lithium-phosphate glasses.

5.3.2.2. The influence of the composition on the bands

Band II (2·4 eV). In the barium-phosphate glasses the intensity of band II (which contains only a small contribution from the relatively weak band III) increases with the barium-oxide concentration (fig. 5.3). This trend is not clearly observable in the series of lithium- (fig. 5.2) and magnesium-phosphate glasses (fig. 5.4) which may be due to differences in the rate of formation of the colour centres caused by secondary effects such as inhomogeneities in composition. In glasses with the composition 0·20 MO . 0·80 $PO_{2·5}$, the intensity of band II increases from magnesium to barium (fig. 5.5).

These effects combined with the fact that the band energy is independent of the metal oxide, support the conclusion that band II is due to a colour centre containing P and O ions only, while the metal ions are involved in the formation of the centres.

Band III (≈ 3 eV). The energy of band III depends on the metal oxide present in the glass (fig. 5.5). A high field strength of the metal ion corresponds to a high band energy (table XIV). Band III was not found in the sodium-phosphate glasses (fig. 5.6). The concentration dependence of the intensity of band III in the magnesium- and lithium-phosphate glasses could not be established unambiguously, as this band is overlapped by band II, but the estimated ratio of the

TABLE XIV

The energy of band III in relation to the field strength of the metal ions involved

metal ion	field strength $2z/a^2$	energy of band III (eV)
Mg^{2+}	1·02(4-coord.)	3·3
Mg^{2+}	0·90(6-coord.)	
Ca^{2+}	0·69	3·2
Sr^{2+}	0·58	3·1
Ba^{2+}	0·51	3·0
Li^+	0·45	3·0
Na^+	0·35	—
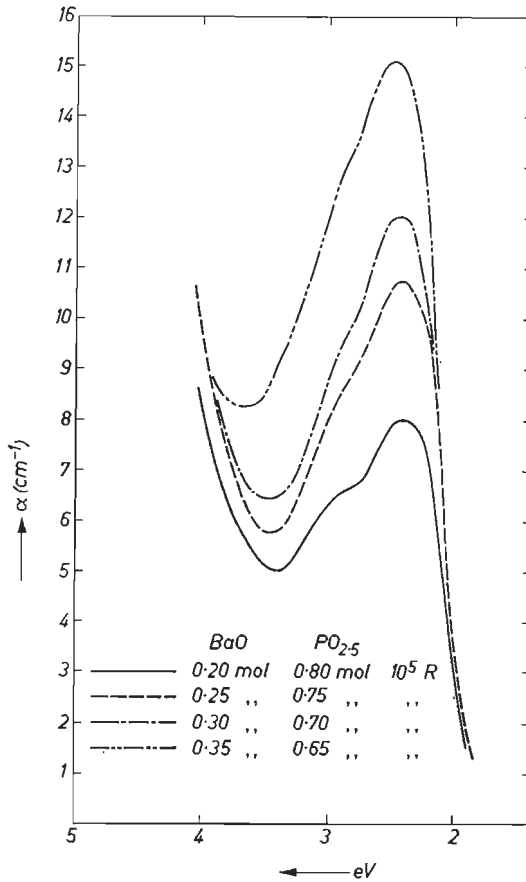
Fig. 5.3. The radiation-induced optical spectra of barium-phosphate glasses.
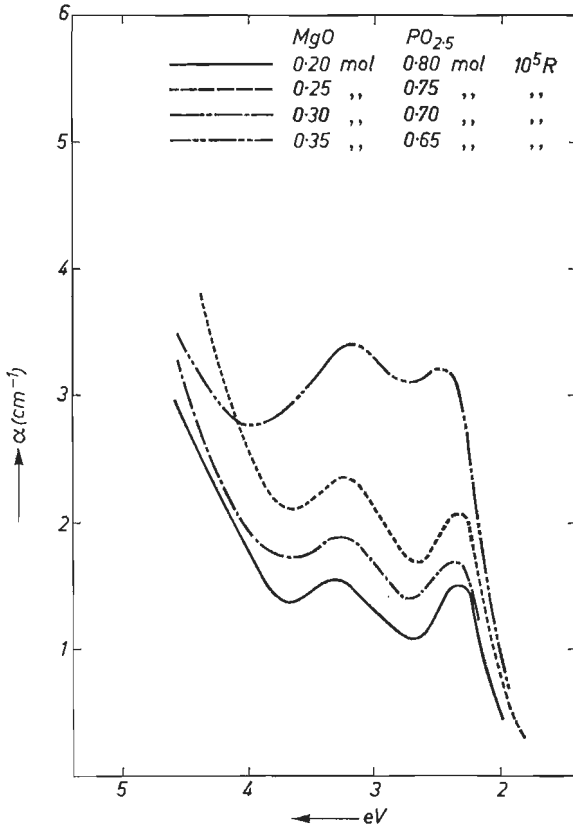
Fig. 5.4. The radiation-induced optical spectra of magnesium-phosphate glasses.

heights (α_{III} and α_{II}) of the bands III and II in the alkaline-earth-phosphate glasses (0·20 MO. 0·80 $PO_{2.5}$) indicates that band III becomes smaller compared with band II as the field strength of the metal ions decreases (table XV). A similar effect is observed with an increase of the barium-oxide concentration in barium-phosphate glasses (fig. 5.3).

From the results obtained so far it may be concluded that the metal ions form part of the band-III colour centres and of their progenitors.

TABLE XV

The ratio α_{III}/α_{II} in glasses of the composition 0·20 MO. 0·80 $PO_{2.5}$

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
α_{III}/α_{II}	1·0	0·7	0·1	0·06
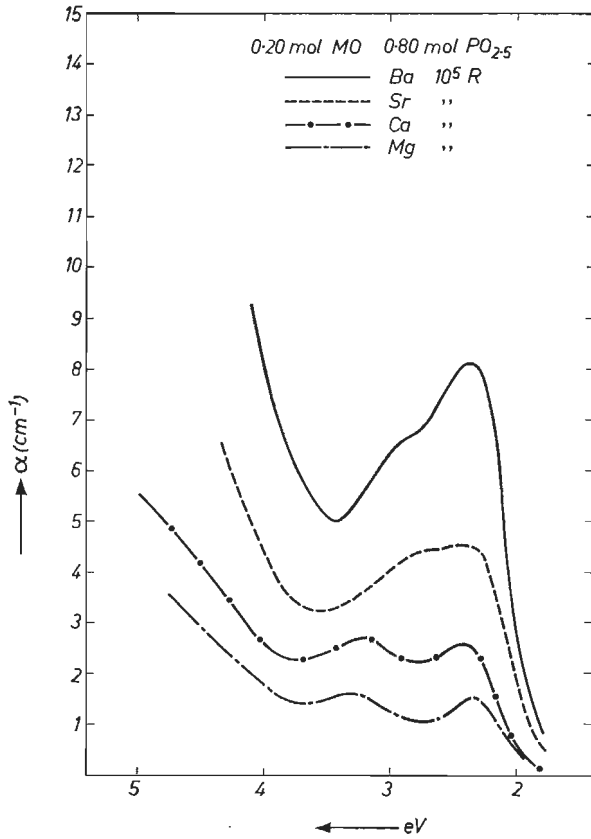
Fig. 5.5. The radiation-induced optical spectra of glasses of the composition 0·20 MO. 0·80 PO$_{2.5}$.

Band IV ($\approx$6 eV). As pointed out, an indication of the intensity of band IV is given by the incline of the absorption curve between 4 and 5 eV. This incline is found to decrease with an increase in the field strength of the metal ions.

5.3.3. *The radiation-induced ESR spectra*

5.3.3.1. The two-band spectrum

All the irradiated phosphate glasses discussed in this chapter show a basic ESR spectrum as given in fig. 5.7a, which is the recorded first-derivative curve of irradiated BeP$_2$O$_6$ glass. The integrated curve (fig. 5.7b) could be resolved into two identical bands, which are somewhat asymmetrical. This resolution was obtained by trial and error. The mean *g*-factor was about 2·009 in the glasses investigated. The hyperfine splitting was somewhat dependent on the metal oxide present (table XVI).

Fig. 5.6. The radiation-induced optical spectra of sodium-phosphate glasses.

Fig. 5.7. The radiation-induced ESR spectrum of BeP_2O_6 glass.
(a) Observed first derivative of the spectrum.
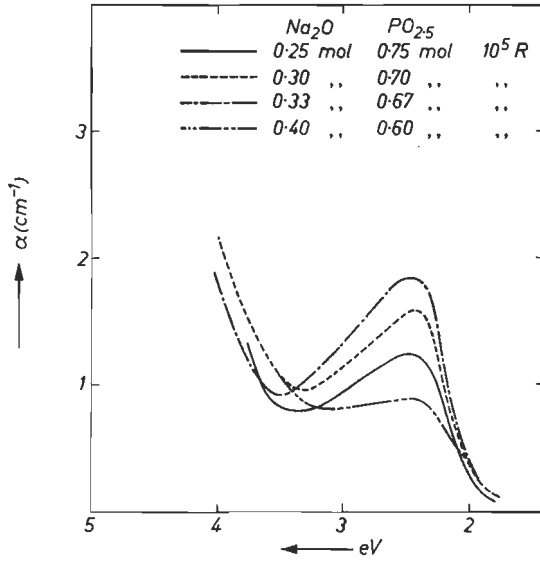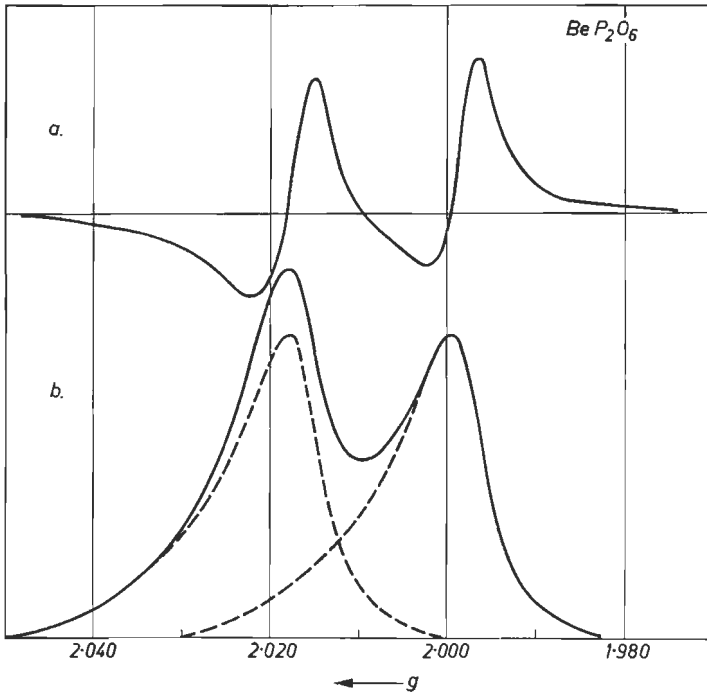(b) Solid curve: integrated curve 5·7 (a); dashed curve: resolved hyperfine bands.

TABLE XVI

The mean g-factor and the hyperfine splitting Δg of the ESR doublet observed in irradiated alkali- and alkaline-earth-phosphate glasses

metal ion	g-factor	hyperfine splitting Δg
Be^{2+}	2·0087	0·018
Mg^{2+}	2·0090	0·021
Ca^{2+}	2·0090	0·023
Sr^{2+}	2·0088	0·023
Ba^{2+}	2·0089	0·023
Li^+	2·0090	0·023

TABLE XVII

Abundance of the isotopes in a glass of composition MP_2O_6

isotope	natural abundance (%)	atom % in glass	nuclear spin
H^1	99·9	1	1/2
P^{31}	100	22	1/2
O^{16}	99·76	66	—
O^{17}	0·04	0·03	5/2
O^{18}	0·20	0·17	—
Be^9	100	11	3/2
Mg^{25}	10·1	1	5/2
Ca^{43}	0·13	0·1	7/2
Sr^{87}	6·96	0·8	9/2
Ba^{135}	6·56	0·7	3/2
Ba^{137}	11·24	1	3/2

The hyperfine splitting into two equal bands must be due to the isotope P^{31} with spin $= 1/2$, as may be concluded from table XVII. The paramagnetic centre producing these two bands may be described as an *electron-hole centre* ($g > 2.0023$) adjacent to a P^{31} nucleus. The hole shows no direct interaction with the metal ions, but beryllium and magnesium ions do have a slight influence on the hyperfine splitting due to the P^{31} nuclei (cf. table XVI).

The form of the ESR spectrum may be represented by eq. (2.11) of sec. 2.3.2 (cf. fig. 5.8) if it is assumed in addition that

$$|A|/g_{||} = |B|/g_{\perp} \quad \text{and} \quad I = 1/2$$

and that a number of line-broadening effects are involved (cf. sec. 2.3.2). This means that the centre experiences an axially symmetrical crystalline field, hence the PO_4 tetrahedron involved will be of axial symmetry.
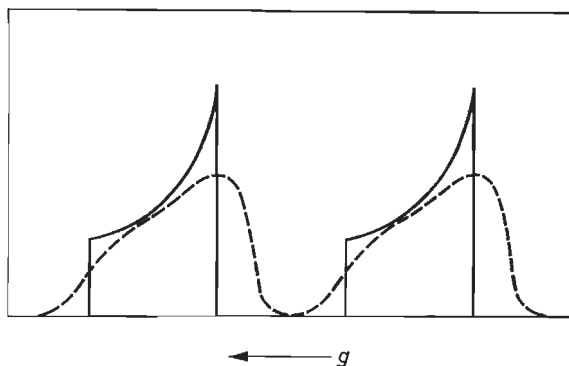

Fig. 5.8. The ESR spectrum of a glass according to eq. (2.16) for $g_{||} > g_{\perp}$, $I = \frac{1}{2}$ and $|A|/g_{||} = |B|/g_{\perp}$.

5.3.3.2. The radiation-induced ESR spectra of glasses with a low concentration of strontium oxide or barium oxide

Glasses with a low concentration of metal oxide are prepared from concentrated H_3PO_4 and the carbonate of the required metal ion. Under the conditions used for the preparation of the phosphate glasses (electrically fired furnace; in air) the glasses with a low concentration of strontium and barium oxide could not be freed from a part of the water, and remained sticky after quenching. Their ESR spectra contained two new bands ($g_1 = 2.009$; $g_2 = 2.003$) and the hyperfine doublet decreased rapidly with the appearance of these bands (fig. 5.9). If dry nitrogen is bubbled through during the melting of a batch of composition 0.15 SrO. 0.85 $PO_{2.5}$ the glass thus obtained is not sticky after cooling and the ESR spectrum shows only very slight traces of the new bands, while the two hyperfine bands show intensities comparable with those in the glasses with a higher strontium-oxide concentration. It is therefore believed that the two new bands are due to the presence of a larger amount of hydrogen ions in these glasses.

5.3.4. Comparison and discussion of the optical- and ESR-absorption spectra

The nature of the colour centres formed upon irradiation in glasses depends on the structural units present in the glass. In phosphate glasses below the
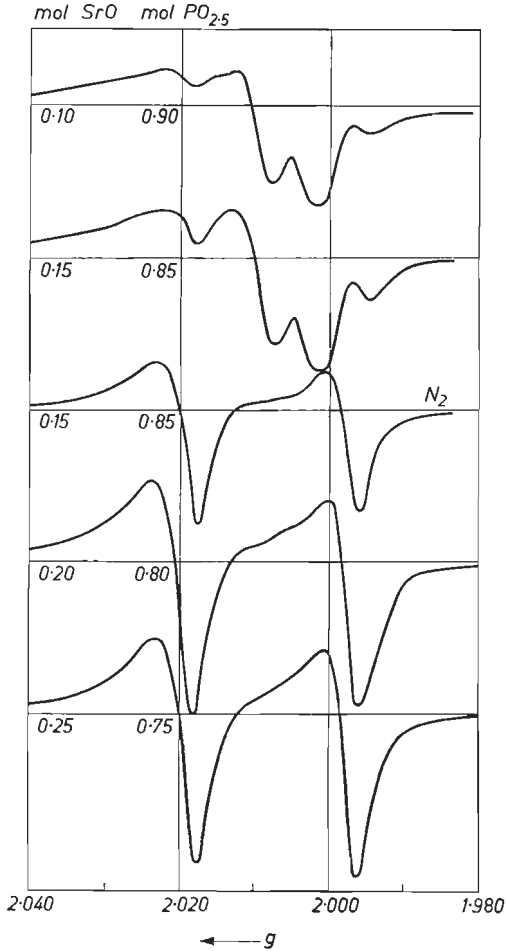
mol SrO   mol PO$_{2.5}$

0·10   0·90

0·15   0·85

0·15   0·85

N$_2$

0·20   0·80

0·25   0·75

2·040   2·020   2·000   1·980

← — g

Fig. 5.9. The radiation-induced ESR spectra of strontium-phosphate glasses.

metaphosphate composition the PO$_4$ tetrahedra form a three-dimensional net-work with additional -O-M-O-bridges. Beyond this composition the glass consists of an assembly of chains of PO$_4$ tetrahedra, cross-linked by -O-M-O bridges. This change has a great influence on many properties of the glasses, especially on those which depend on the bulk rigidity of the network. The properties of the colour centres, however, do not depend on the bulk rigidity of the glass structure but are determined by the local rigidity in the structural units. This explains the absence of changes in the properties of the colour-centre bands at the metaphosphate composition. The ESR doublet which was found in all the phosphate glasses investigated (figs 5.7, 5.9 and 5.10) is believed to be due to an electron-hole centre adjacent to a P^{31} nucleus in a crystal field of axial symmetry. A simple model of such a colour centre is an electron hole on an

oxygen ion which is singly bonded to one phosphorus ion only. The mechanism of formation of such a centre may be described as follows. Several types of oxygen may be present in the structure units of the phosphate glasses (cf. sec. 5.2.6). One of the units can be described as a hybrid between type II and type III, the character of the hybrid depending on the field strength of the metal ion involved.
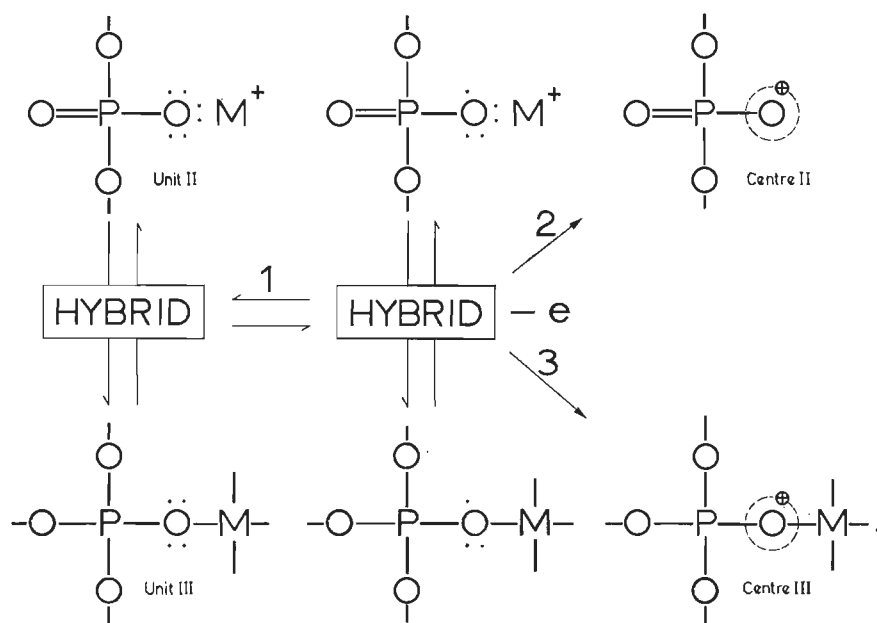
Upon irradiation the oxygen ion adjacent to the metal ion may lose an electron. The positively charged hybrid structure thus obtained may be neutralised in three different ways:

(1) an electron is captured: the original structure is restored;
(2) the metal ion moves to some other site in the network: a colour centre of type II is formed;
(3) a redistribution of the valency electrons takes place: a colour centre of type III is formed.

Whether colour centres of type II or type III are formed depends on the bonding character of the metal ions. If the field strength of the metal ion involved is small, in other words if the hybrid structure has a predominantly ionic character (unit II) the metal ion may be moved to another site in the network more easily (reaction 2) than in the case of a metal ion with a higher field strength, which gives the hybrid structure a predominantly covalent character. In the latter case a redistribution of the valency electrons will be favoured, colour centres of type III being formed (reaction 3).

These conditions for the formation of the two types of hole centres agree with
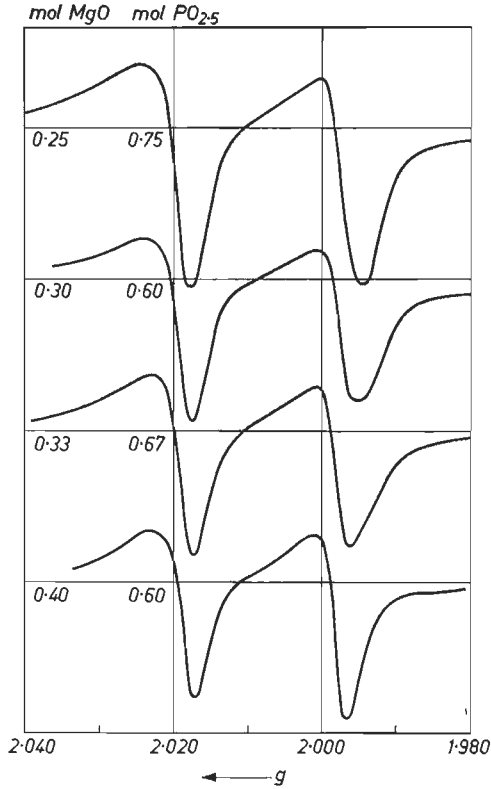
Fig. 5.10. The radiation-induced ESR spectra of magnesium-phosphate glasses.

the properties of the induced optical bands II and III (cf. sec. 5.3.2.2). An assignment of band II (2·4 eV) to colour centres of type II, and of band III ($\approx$3eV) to colour centres of type III, seems justified as it also agrees with the conditions that the band-III colour centres *do* contain metal ions and the band-II colour centres *do not*.

The formation of type-II centres is not only dependent on the field strength of the metal ions but also on the coherence of the network. From the optical-absorption spectra of the barium-borate glasses (fig. 5.3) it may be concluded that an increase of the BaO concentrations, which lowers the degree of coherence, favours the formation of centres of type II with respect to the number of centres of type III.

Now can the hyperfine doublet in the ESR spectra be assigned to both types of colour centres or to only one of the two types? Before an answer can be given to this question, a more detailed discussion of the ESR spectra will be necessary. The doublet bands show a slight anisotropy, which is due to a crystal field of

axial symmetry around the hole centre. The structure of the colour centres of type II does not show an axis of symmetry. However, it is conceivable that a non-bridging oxygen ion with electron hole (centre II) can be converted into a doubly bonded oxygen ion and vice versa by the jumping of one electron:

$$
\begin{array}{c}
\text{P} \\
\vdots \\
\text{:O:} \\
\text{P :O: P}^{\oplus}\text{:O}^{\ominus}\text{:}\,. \\
\text{:O}\,\diagup \\
\end{array}
$$
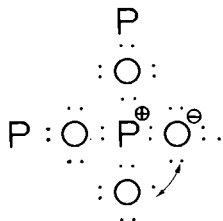
If the jumping of the electron occurs with a high frequency, the ESR equipment will "see" this centre as an axially symmetrical one.

This model is in agreement with the conclusions of Schreurs and Tucker [7]), who calculated from the hyperfine splitting that the orbit of the electron hole around the P^{31} nucleus must be of the π-type, which implies that the hyperfine interaction is of the dipolar type. The hyperfine splitting of the doublet of beryllium- and magnesium-phosphate glasses is slightly less than that of the barium- and strontium-phosphate glasses (table XVI). It is believed that ions with a high field strength in the direct environment of the centres may influence the hyperfine interaction between the electron hole and the phosphorus nucleus.

Apart from a phosphorus ion, the colour centres of type III contain a metal ion adjacent to the oxygen ion with the captured hole. It may therefore be expected that the hole will interact with the phosphorus as well as the metal nucleus, giving a larger number of bands. The number of bands due to hyperfine splitting is given by $(2I_1 + 1)(2I_2 + 1)$, where I_1 and I_2 are the nuclear spins of the phosphorus and metal nuclei, respectively. In the case of an axially symmetrical crystal field, this number may be doubled. An unsymmetrical crystal field may give rise to three times this number. Broadening effects and the low intensity of each band may cause the ESR signal of this hole centre to be masked by the doublet due to the centres of type II, which is always observed. This may explain the absence of a *specific* ESR spectrum of colour centres of type III. However, this apparent absence may also be explained in the following way. The interaction between the electron hole and the metal nucleus will be weaker than the interaction between the hole and the phosphorus nucleus. This difference in interaction may give rise to a set of P^{31} energy levels, each of which is split into $(2I_2 + 1)$ sub-levels due to the metal nucleus; these sub-levels will then be located so close to each other that they cannot be resolved, which means that centres of type III will show the same ESR spectrum as centres of type II. The small change in hyperfine splitting of the doublet is probably due to a weak interaction with the metal ions of a high field strength.

The assignment of the optical band IV ($\approx$ 6 eV) must be a tentative one, because of the rather vague experimental data on this band. It could be established that the intensity of band IV tends to decrease with increasing field strength of the metal ions. It is assumed that this band is due to an oxygen vacancy in a PO_4 tetrahedron, which has trapped two electrons (colour centre of type IV). A number of facts can be given which may support this.

(1) In glasses with a low content of metal ions with low field strength, structural units may be present of almost pure type IV (doubly bonded oxygen). If the colour centres of type IV are formed according to the equation
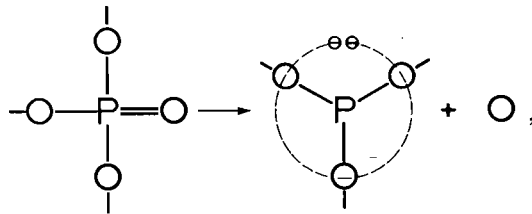
their number will decrease with the number of units of type IV. As pointed out before (cf. sec. 5.2.6), an increase in the field strength of the metal ions will tend to convert units of type IV into the hybrid between type II and type III. This may explain the observed decrease of the intensity of band IV with an increase in the field strength of the metal ions.

(2) The captured pair of electrons makes this centre undetectable by means of ESR spectrometry. The ESR spectra contained no band with a g-factor smaller than 2·0023, which would have indicated the presence of an unpaired-electron centre in the glass.

(3) In fused silica an optical colour-centre band was observed at 5·8 eV, which was attributed to an oxygen vacancy in an SiO_4 tetrahedron which had captured one electron [23,24]. This centre (with an unpaired electron) could be detected by means of ESR measurements. The energy of the optical-absorption band of centres of this type is of the same order of magnitude as the band energy of the centres of type IV.

5.3.5. *Comparison of the proposed colour-centre models with those of other authors*

Karapetyan and Yudin [4] proposed models for the structure of an electron centre and an electron-hole centre which both disagree with the models presented in this thesis. Although the ESR doublet in their spectra has a g-factor greater than 2·0023, they assigned it to an electron captured on a phosphorus ion. This assignment is very likely to be incorrect.

Tucker [5,7] assigned the ESR doublet to a hole trapped in a π-bonding orbital in a PO_4 group, which agrees with the model proposed in this paper. Tucker,

like Karapetyan and Yudin, correlated the ESR doublet with the optical bands II (2·4 eV) and III ($\approx$3 eV). This correlation agrees with the one that has been proposed in this thesis, if it is assumed that the second explanation given in sec. 5.3.4 for the absence of a *specific* ESR spectrum of the colour centres of type III is correct. The model given by Karapetyan and Yudin for the colour centres causing the far-u.v. absorption ($\approx$6 eV) is a hole trapped on a non-bridging oxygen ion as opposed to the captured electron pair in a doubly bonded non-bridging oxygen vacancy proposed in the previous section.

5.4. Conclusions

Four types of structural units (I, II, III, IV) may be distinguished in phosphate glasses (table XVIII). It is believed that the metal ions are bound to the glass network by an oxygen ion in a partly ionic (type II), partly covalent way (type III), which is represented by a hybrid structure between the units of types II and III. Metal ions with a low field strength will be bonded in a hybrid structure of a predominantly ionic character, while metal ions with a high field strength will be bonded in a hybrid structure of a predominantly covalent character.

The three major colour centres could be correlated to the structure units II, III and IV. For the sake of clarity the colour centres and the induced optical bands involved have also been numbered II, III and IV; no colour centre has been observed that could be correlated to structural unit I.

A colour centre of type II may be described as an electron hole captured on a singly bonded non-bridging oxygen ion (unit II). However, this hole may jump to an adjacent doubly bonded non-bridging oxygen ion which results in a structure equivalent to the initial one. From the axially symmetrical shape of the ESR band it may be concluded that this jumping occurs with a high frequency, so that the ESR equipment "sees" the hole centre as an axially symmetrical one.

A colour centre of type III may be described as an electron hole captured on an oxygen ion bonded to a phosphorus and a metal ion (unit III). This model also shows an axis of symmetry, so that theoretically the asymmetrical ESR doublet might equally well be assigned to this colour centre, if the hyperfine interaction of the metal nucleus is weak compared with that of the phosphorus nucleus. However, it can be shown to be likely that this centre does not give an experimentally observable ESR spectrum, owing to the fact that the electron-spin resonance is split up in many weak (anisotropic) bands by the interaction with the phosphorus and the metal nucleus, these bands being obscured by the strong doublet practically always found in phosphate glasses.

A colour centre of type IV may be described as an oxygen vacancy in a PO_4 group which has captured two electrons. This centre does not contain an unpaired electron, which explains the absence of a corresponding ESR spectrum. It may be concluded from the radiation-induced optical spectra that these cen-

TABLE XVIII

Survey of the types of structural units in phosphate glasses and the types of radiation-induced colour centres, with the corresponding optical- and ESR-absorption bands

| structural unit | | induced absorption bands | | | type of colour centres formed upon irradiation | | occurrence in phosphate glasses in order of decreasing number |
| | | optical | | ESR | | | |
type	structure	type	energy (eV)	mean g-factor	type	model	
I	=P—O—P=	—	—	—	—	—	all glasses
II	=P—O M$^{+(+)}$	II	2·4	2·009 doublet $\Delta g \sim 0·02$	II	O=P—Ö (model)	Ba Na, Li Sr Ca Mg (Be)
III	HYBRID ; —P—O—M—	III	? 3·3 3·2 3·1 3·0 3·0 —	2·009 doublet $\Delta g \sim 0·02$,, ,, ,,	III	—O—P—Ö—M— (model)	Be Mg Ca Sr Ba Li Na
IV	—P=O	IV	~6	—	IV	(model)	Ba Sr Ca Mg Be
—	?	—	—	2·009 2·003 singlets	—	?	in strontium and barium-containing glasses with a high OH content and $x < 0·20$.

tres are correlated with the presence of doubly bonded non-bridging oxygen ions (unit IV).

Apart from the above major types of colour centres in phosphate glasses, a number of centres of as yet unknown structure are believed to be formed in strontium- and barium-phosphate glasses at low metal-oxide concentrations. These glasses contain a larger amount of "water", which has been shown to be responsible for the formation of these types of centres.

In irradiated phosphate glasses containing metal ions with a low field strength, the amounts of colour centres of type II and IV are greater and of type III are smaller (even falling to zero in sodium-phosphate glasses) than in glasses containing metal ions with a higher field strength. These trends agree with the hypothesis for the structure of phosphate glasses given above.

In the barium-phosphate glasses it was found that increasing the barium-oxide concentration increased the amount of type-II colour centres compared to that of type-III centres, which indicates that the formation of type-II centres is favoured by a lower degree of coherence of the network.

It may be concluded further that any effect that increases the ration α_{II}/α_{III} also increases the number of type-IV colour centres. Such an effect is a decrease in the field strength of the metal ions. This means that a decrease in the field strength of the metal ions gives the *hybrid* structure more of an ionic character, in other words, that the type-III units will be converted into units of type II and IV.

Many properties of phosphate glasses show a marked change at the metaphosphate composition. This has been explained by the change from a three-dimensional network to an assembly of chains of PO_4 tetrahedra cross-linked by O-M-O bridges. In general the properties that show this effect, are related to the bulk rigidity of the glass network. The colour centres, however, are not related to the bulk rigidity, but to the local rigidity of the structural units of the network. These units only alter gradually as the composition changes. This doubtlessly accounts for the absence of a sudden change in the properties of the colour centres at the metaphosphate composition.

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6. COLOUR CENTRES IN BOROPHOSPHATE GLASSES

6.1. Introduction

In this chapter an attempt will be made to obtain some information about the structure of the borophosphate glasses by means of a study of the radiation-induced colour centres in these glasses, using knowledge of colour centres in borate and phosphate glasses, described in the preceding chapters.

6.2. The structure of borophosphate glasses

It has been found that the crystalline compounds of the composition $M^{III}M^{V}O_4$, such as BPO_4, $BAsO_4$, $AlAsO_4$ and BVO_4, are isostructural with crystalline silica. So far pure $BAsO_4$ and BVO_4 and also mixtures of $BAsO_4$ and $AlAsO_4$ have been obtained in the vitreous state [1]). By means of infrared spectroscopy it has been shown that the boron ions in these glasses are three-fold coordinated by oxygen ions. Therefore, the analogy in structure between crystalline $BM^{V}O_4$ and SiO_2, does not hold for these compounds in the vitreous state. This assumption could not be verified for BPO_4 since this compound could not be obtained in the vitreous state.

If a certain amount of metal oxide is added, borophosphate glasses can be formed. It is impossible to draw conclusions concerning the coordination number of the boron ions from the infrared spectra of these glasses, as the determining B-O vibration bands are obscured by other bands originating from e.g. P-O vibrations.

In a study on the durability of phosphate glasses containing boron oxide Kreidl and Weil [2]) assumed that in these glasses BPO_4 groups with a structure similar to that of crystalline BPO_4 are present.

In his study on glasses in the system Na_2O-B_2O_3-P_2O_5 (fig. 6.1) Takahashi [3]) also ascribed the relatively high durability and transformation temperature to the presence of BPO_4 groups with a structure analogous to that in the crystalline compound, made up of BO_4 and PO_4 groups both with four bridging oxygen ions, the excess of negative charge on the BO_4 group being compensated by the excess of positive charge on the PO_4 group.

It therefore seems justified to conclude that, apart from the typical structural units present in borate and phosphate glasses, a specific structural unit may be found in borophosphate glasses, consisting of a boron ion in tetrahedral co-ordination with four bridging oxygen ions, the excess of negative charge being compensated by an adjacent phosphorus ion in tetrahedral coordination with four singly bonded oxygen ions (cf. table XIX).

These units will be referred to as units of type c_P, where c, as in the borate glasses, stands for a BO_4 group and the subscript P indicates the nature of the

TABLE XIX

Types of structural units in borophosphate glasses
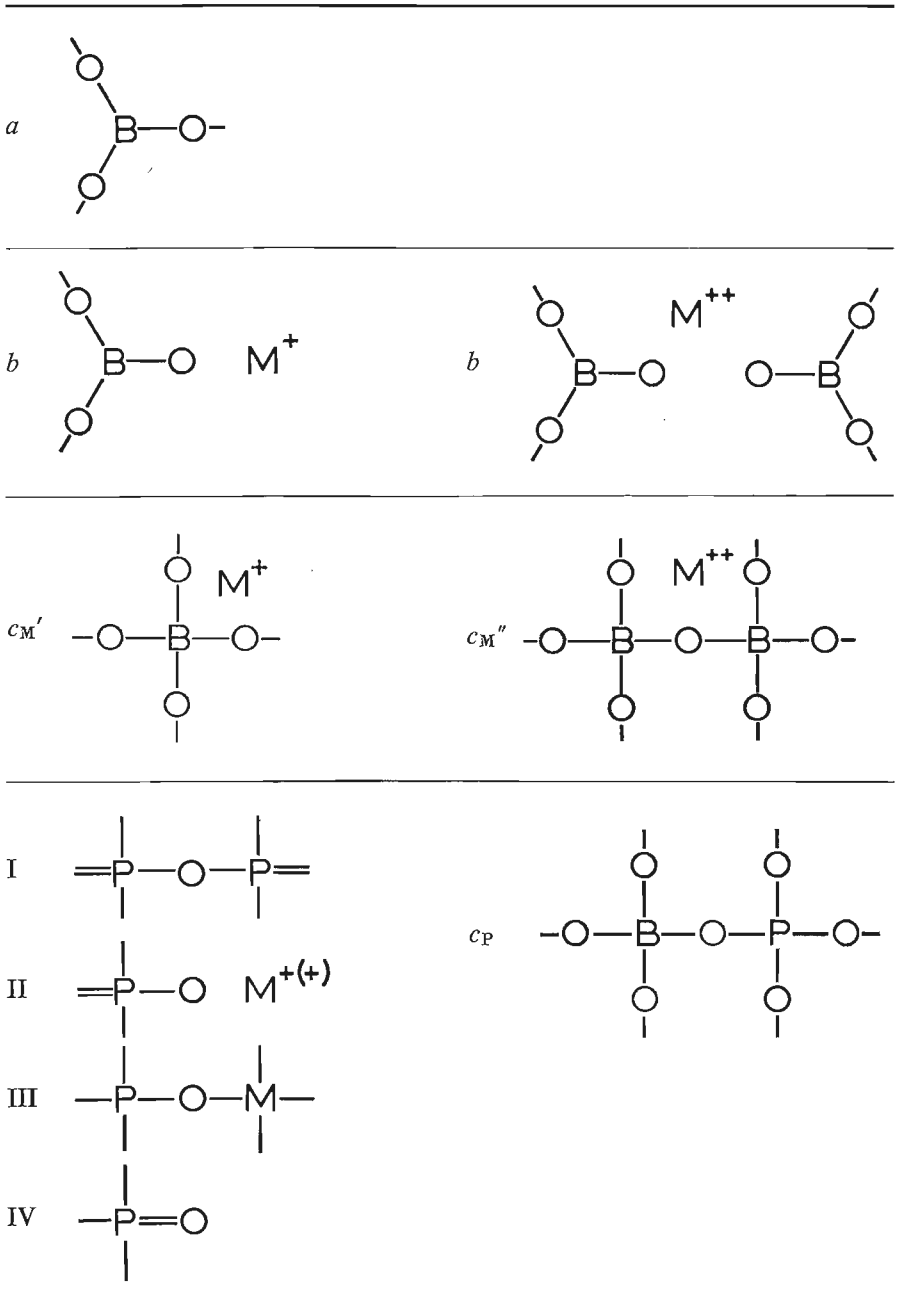
charge compensator, in this case a PO_4 group. For the sake of clearness, the BO_4 groups occurring in borate glasses will hereafter be referred to as units of the types c_M' and c_M'', where M indicates that the charge compensator consists of an alkali or an alkaline-earth ion, and where the single and the double accent refers to the number of BO_4 groups.

It should be remarked that Takahashi did not take into account the probable formation of BO_4 groups as found in the alkali-borate glasses (c_M'-units).

For the discussions given below it is useful to modify the definitions of the parameters N_4 and X somewhat, so that they are adapted to the specific types of structural units that may be expected in the borophosphate glasses. The modified definitions are as follows:

$_{tot}N_4$ = the total number of boron ions in tetrahedral coordination relative to the total number of network-forming ions (in this case: the total number of boron and phosphorus ions); $\qquad$ (6.1)

$$_M N_4 = \frac{\text{the total number of } BO_4 \text{ groups of the types } c_M' \text{ and } c_M''}{\text{the total number of network-forming ions}} ; \qquad (6.2)$$

$$_P N_4 = \frac{\text{the total number of } BO_4 \text{ groups of type } c_P}{\text{the total number of network-forming ions}} ; \qquad (6.3)$$

X' = the mean number of singly bonded non-bridging oxygen ions per polyhedron; $\qquad$ (6.4)

X'' = the mean number of doubly bonded non-bridging oxygen ions per polyhedron. $\qquad$ (6.5)

If the composition of the borophosphate glass is given by $x\,M_{(2)}O.y\,BO_{1.5}.(1-x-y)\,PO_{2.5}$, the following equations hold:

and
$$_M N_4 + X' = 2x/(1-x) \qquad (6.6)$$

$$X'' + _P N_4 = [1-(x+y)]/(1-x) \qquad (6.7)$$

(if M has a low ionic field strength).
From the previous definitions it follows:

$$_{tot}N_4 = _M N_4 + _P N_4 \qquad (6.8)$$

and
$$_{tot}X = X' + X''. \qquad (6.9)$$

Hence

$$Y = 3 + _M N_4 + 2\,_P N_4 - X' = 3 + 2\,_{tot}N_4 - 2x/(1-x) \qquad (6.10)$$

and
$$Z = _{tot}X + Y = 4 + _{tot}N_4 - y/(1-x). \qquad (6.11)$$

6.3. Glasses in the system x Na$_2$O. y BO$_{1\cdot5}$. (1-x-y) PO$_{2\cdot5}$

6.3.1. *The glass-forming region*

According to Takahashi [3]) the glass-forming region of this system may be represented by the hatched area in fig. 6.1. It must be emphasized, however, that the limits of this region depend somewhat on the preparation conditions.
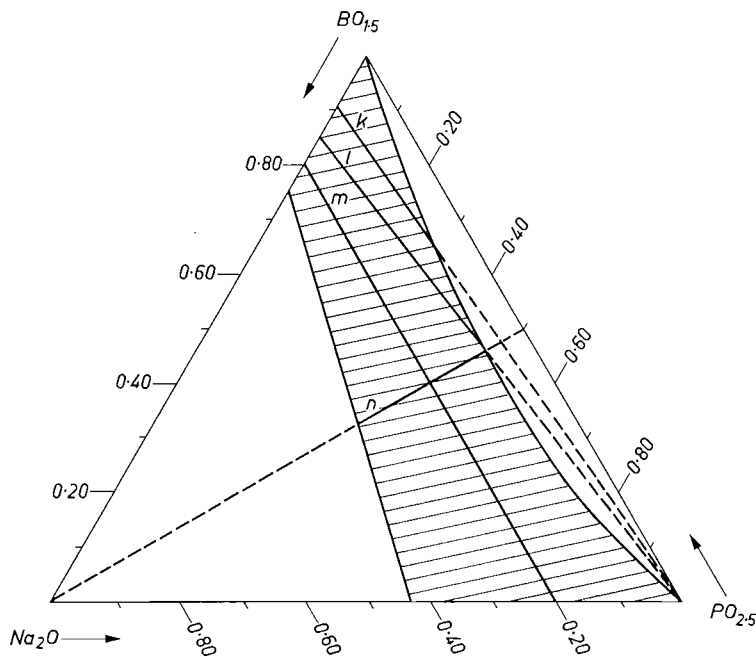

Fig. 6.1. Glass-forming region (hatched area) in the ternary system sodium oxide-boric oxide-phosphorus pentoxide, after Takahashi [3]).

A high rate of cooling of the melt [1]) and an increased amount of structurally bound "water" in the glass [4]) will enlarge the glass-forming region.

6.3.2. *Results of recent NMR measurements*

In sec. 3.2.4 it has been shown that nuclear-magnetic-resonance spectra of boron-containing glasses can give information about the number of tetrahedrally coordinated boron ions. Bray [5,6]) and Krogh-Moe [7]) used this method on alkali-borate glasses of varying composition. The method has also been applied to four series of glasses in the system Na$_2$O-BO$_{1\cdot5}$-PO$_{2\cdot5}$ [8]), represented by the four lines k, l, m and n in fig. 6.1. The values of $_{tot}N_4$ (eq. 6.1) for boro-phosphate glasses have also been determined in this way here, the values of $_MN_4$ for alkali-borate glasses given by eq. (3.13) (cf. sec. 3.2.5) being used as standard values. The location of the bands in the NMR spectra is only influenced

by the nearest neighbours of the B^{11} nuclei, viz. oxygen ions. The next-nearest neighbours (the surrounding boron, phosphorus and metal ions) only show a slight influence on the band width. Hence the NMR method can distinguish between threefold- and fourfold-coordinated boron ions, but does not distinguish between the two types of BO_4 groups c_M' and c_P.

The results of these measurements are represented in fig. 6.2. At compositions on the right-hand side of the broken, vertical line in figs 6.2a and 6.2b, representing the $_{tot}N_4$ values of the series k and l, respectively, no glass formation takes place. However, if glasses could be prepared in this region, the $_{tot}N_4$ vs composition curve, after passing through a maximum, ought to decrease to zero for pure P_2O_5 glass e.g. as indicated in these two figures. At the boric-oxide-rich side of these figures the $_{tot}N_4$ curve decreases approximately linearly with an increase in the $PO_{2.5}$ concentration. At about 0·15 mol. and 0·23 mol. $PO_{2.5}$ for series k and l, respectively, the $_{tot}N_4$ curve deviates from this approximately linear relationship. The values of $_{tot}N_4$ for the glasses of series m and n are represented in figs 6.2c and 6.2d. The shape of the $_{tot}N_4$ curves will be explained in the following section.

6.3.3. A hypothesis for the structure of sodium-borophosphate glasses

In a sodium-borate glass the excess of oxygen ions introduced by the sodium oxide may be taken up in the glass network as a fourth bridging oxygen ion bound to a boron ion, forming a structural unit of type c'_M, or as a non-bridging oxygen ion in a BO_3 group, forming a b-unit (cf. table XIX). The amounts of these two types of units are governed by the equilibrium
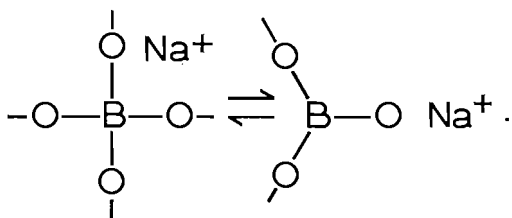
It has been shown in sec. 3.2.5 that the relative number of boron ions in tetrahedral coordination may be represented by

$$_M N_4 = [x/(1-x)]\{1 + \exp(11·5\,x - 4·8)\}^{-1}, \qquad (6.12)$$

if the composition is given as $x\,Na_2O.(1-x)\,B_2O_3$. In this chapter the compositions of the sodium-borophosphate glasses are given by $x\,Na_2O.\,y\,BO_{1.5}.(1-x-y)\,PO_{2.5}$. The pure borate glasses are found in this ternary system, where $x + y = 1$ and the quantity $_M N_4$ is then given by eq. (6.13):

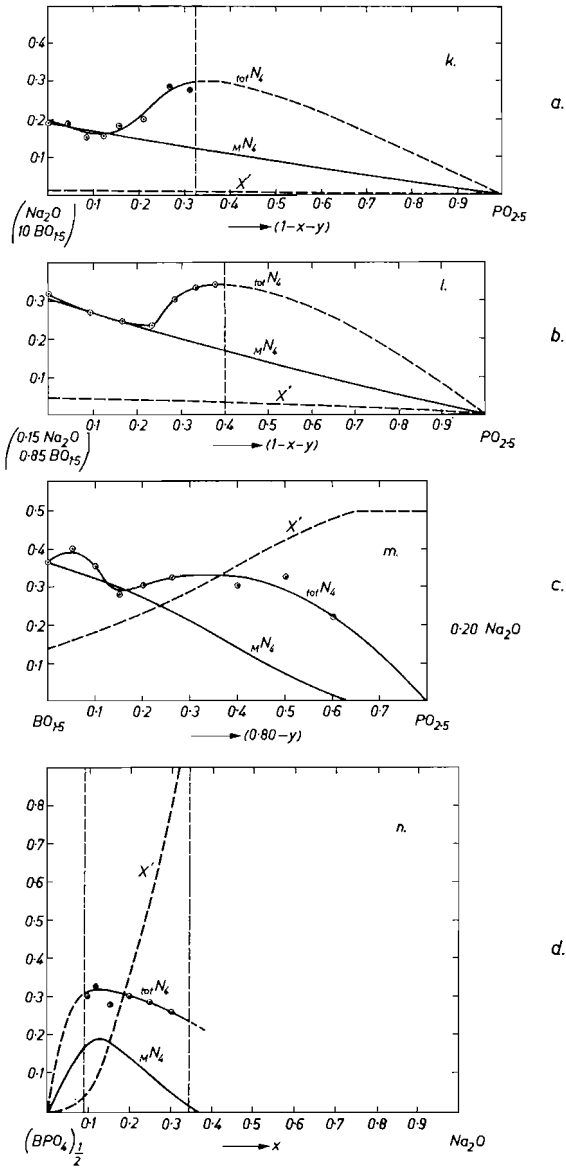$$_M N_{4(x+y=1)} = (2x/y)\{1 + \exp[11·5\,.\,2x/(2x + y) - 4·8]\}^{-1}. \qquad (6.13)$$

Fig. 6.2. $_{tot}N_4$, $_M N_4$ and X' as a function of the composition in four series of glasses in the system Na_2O-$BO_{1.5}$-$PO_{2.5}$. In the figures, $_P N_4 = {}_{tot}N_4 - {}_M N_4$.
(a) line k : Na_2O. $10\ BO_{1.5}$. $p\ PO_{2.5}$,
(b) line l : $0.15\ Na_2O$. $0.85\ BO_{1.5}$. $q\ PO_{2.5}$,
(c) line m : $0.20\ Na_2O$. $y\ BO_{1.5}$. $(0.80 - y)PO_{2.5}$,
(d) line n : $x\ Na_2O$. $(1 - x)\ (BPO_4)_{0.5}$.

In a sodium-borophosphate glass the excess oxygen ions introduced by the sodium oxide may be taken up in the network in a way similar to that in the borate glasses: in structural units of the types c_M' and b; however, the singly bonded non-bridging oxygen ions as found in the b-units may now also be bound to a phosphorus ion. As the sodium ions have a low ionic field strength, the unit formed will be of type II rather than of type III, in other words the sodium ion will be bound to the oxygen ion ionically rather than covalently.

The amounts of the three types of structural units will now be determined by an equilibrium between units of type c_M' on the one hand and units of the types b and II on the other hand.

$$c_M'\text{-unit} \qquad\qquad \text{unit II}/b\text{-unit}$$
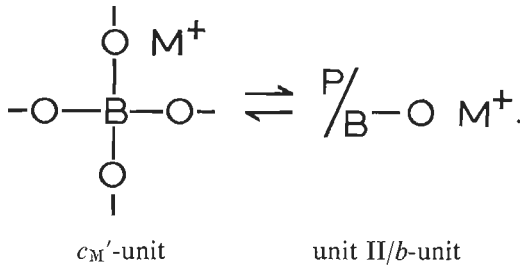
If it is assumed that this equilibrium is not influenced by the ratio of the amounts of units of type b and type II the number of units of type c_M' relatively to the total number of boron ions in the borophosphate glass remains constant for a given value of x/y. This may be expressed by

$$[(1 - x)/y] \, _MN_4 = \, _MN_{4(x+y=1)} = \text{constant} \quad (\text{for } x/y = \text{constant}). \qquad (6.14)$$

Combining eq. (6.13), which is valid when $x + y = 1$, with eq. (6.14) a general relation is found for $_MN_4$ in alkali-borophosphate glasses:

$$_MN_4 = [2x/(1 - x)] \{1 + \exp [11 \cdot 5 . 2x/(2x + y) - 4 \cdot 8]\}^{-1} . \qquad (6.15)$$

It follows from eqs (6.6) and (6.15) that

$$X' = [2x/(1 - x)] \left[1 - \{1 + \exp [11 \cdot 5 . 2x/(2x + y) - 4 \cdot 8]\}^{-1}\right]. \qquad (6.16)$$

In sec. 3.2.5 it has been pointed out that eq. (6.12) describes the experimental results only in the range $Na_2O/B_2O_3 \leqslant 1 \cdot 5$. This means that eqs (6.13), (6.15) and (6.16) are valid only for $x/y \leqslant 3/4$. It is experimentally found in borate glasses that for $x/y > 3/4$ the quantity $_MN_{4(x+y=1)}$ decreases approximately linearly with increasing x and becomes zero for $x = 0 \cdot 54$. The values of $_MN_4$ in borophosphate glasses for $x > 3/4$ can be found by applying eq. (6.14) to the value of $_MN_{4(x+y=1)}$ in this range. In fig. 6.3 the quantities $_MN_4$ and $(_MN_4 + X')$ are represented for the glass-forming region of the system $Na_2O\text{-}BO_{1 \cdot 5}\text{-}PO_{2 \cdot 5}$. The saddle-shaped surface converging to the point where $x + y = 0$ (pure $PO_{2 \cdot 5}$ glass) represents the values of $_MN_4$. The slightly curved

surface emerging from the line $BO_{1.5}$-$PO_{2.5}$ gives the values of $_MN_4 + X' = 2x/(1 - x)$.

Apart from the formation of BO_4 groups of type c_M' upon addition of sodium oxide, BO_4 groups of type c_P may be formed upon the addition of phosphorus pentoxide. The total amount of the units of both types, which is represented by the quantity $_{tot}N_4$, has been measured by means of nuclear magnetic resonance as described in the previous section.

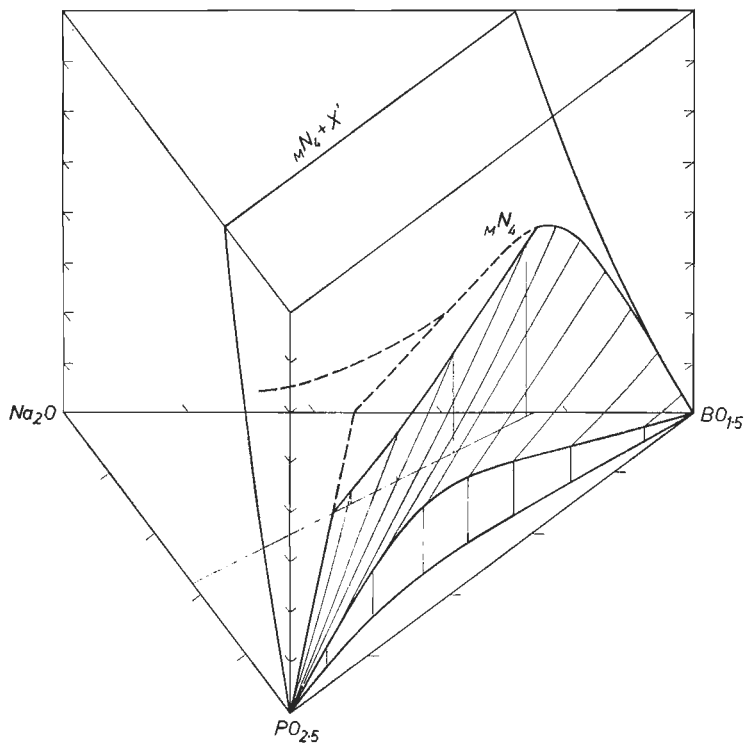Fig. 6.3. A three-dimensional representation of the value of $_MN_4$ as a function of the composition of glasses in the system Na_2O-$BO_{1.5}$-$PO_{2.5}$.

In two series of glasses in the system Na_2O-$BO_{1.5}$-$PO_{2.5}$ with contant values of x/y (line k in fig. 6.1: $x/y = 1/10$; line l in fig. 6.1: $x/y = 3/17$) the experimental $_{tot}N_4$ curves follow the theoretical $_MN_4$ curves given by eq. (6.14), up to a $PO_{2.5}$ concentration of 0·15 and 0·23 mol., respectively. At higher $PO_{2.5}$ concentrations the $_{tot}N_4$ curves deviate from these theoretical values (figs 6.2a and 6.2b). Beyond the compositions given by the broken vertical lines no NMR data could be obtained as these compositions lie outside the glass-forming region. If glasses could be made here, the $_{tot}N_4$ curves ought to pass through a maximum and decrease to zero for $x + y = 0$, i.e. for a glass consisting of pure phos-

phorus pentoxide. These curves may be interpreted as follows in terms of the proposed structural hypothesis. In glasses with a low $PO_{2.5}$ concentration, BO_4 groups of type c_M' *only* are present. At higher concentrations BO_4 groups of both type c_M' and type c_P are formed. The experimental $_{tot}N_4$ and the theoretical $_M N_4$ curves for another two series of glasses in this system are given in figs 6.2c (line m) and 6.2d (line n). In fig. 6.2c the $_{tot}N_4$ curve lies close to the theoretical $_M N_4$ curve for low $PO_{2.5}$ concentrations and deviates at higher concentrations as found for the series k and l in figs 6.2a and 6.2b. In fig. 6.2d where the ratio $BO_{1.5}/PO_{2.5} = 1$ the $_{tot}N_4$ values are higher than the theoretical $_M N_4$ values.

The NMR results for the four series k, l, m and n and eq. (6.15) have been used to plot contours of equal $_{tot}N_4$ and of equal $_P N_4$ (figs 6.4 and 6.5). The proposition that $_{tot}N_4 = 0$ for the hypothetical glasses with $x = 0$ (no sodium oxide) is based on the facts that $_M N_4 = 0$ for $x = 0$ by definition and that $_P N_4 = 0$ for $x = 0$ in the similar glass of composition $BAsO_4$, as has been found by means of infrared spectroscopy [1]), and in glasses consisting of pure B_2O_3 and P_2O_5, respectively.

Takahashi measured the chemical durability and the transformation temperature of four series of glasses in the system Na_2O-$BO_{1.5}$-$PO_{2.5}$ with $Na_2O/PO_{2.5}$
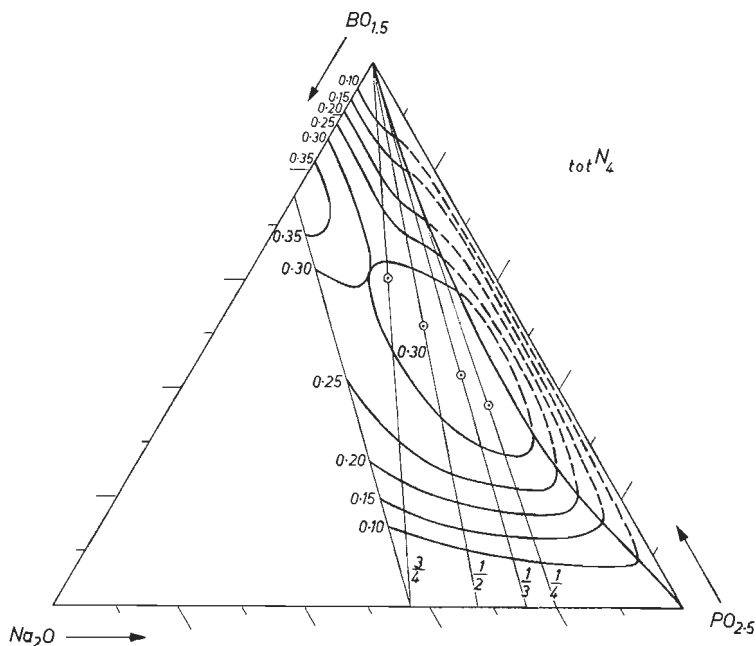
Fig. 6.4. $_{tot}N_4$ contours in the glass-forming region of the system Na_2O-$BO_{1.5}$-$PO_{2.5}$. $\odot$ = compositions where the transformation temperature T_g reaches a maximum, after Takahashi [3]).
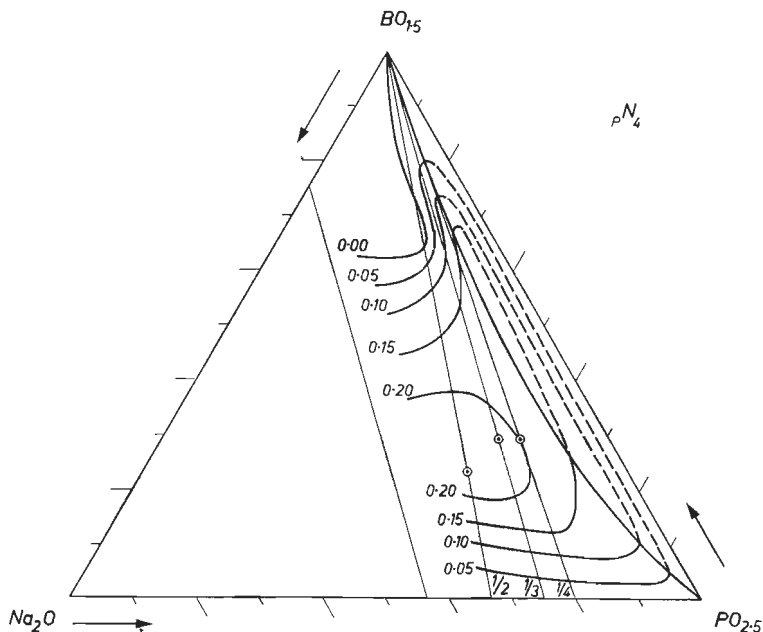
Fig. 6.5. $_pN_4$ contours in the glass-forming region of the system $Na_2O-BO_{1\cdot5}-PO_{2\cdot5}$. ⊙ = compositions where the chemical durability reaches a maximum, after Takahashi [3]).

ratios of 3/4, 1/2, 1/3 and 1/4, respectively. The transformation temperature depends on the coherence of the network, which is favoured by the presence of units of the types c_M' and c_P. The compositions of the four series are represented by four lines in fig. 6.4. On each line the composition where the transformation temperature is maximum is indicated by a circle. These maxima are indeed found in a region where the numbers of units of the types c_M' and c_P given by the parameter $_{tot}N_4$ are maximum. The chemical durability does not specifically depend on the coherence of the network, but on the solubility of the various structural units present in the glass. In fig. 6.5 the compositions where the durability is maximum in each series, are represented by circles. These compositions lie in the region where $_pN_4$ is maximum. It follows that the structural units of type c_P are attacked by water less than the other units in these glasses. It is known from the crystalline compounds that BPO_4 is indeed less soluble in water than its constituents B_2O_3 and P_2O_5, which supports the conclusion given above.

It may be concluded that the proposed hypothesis for the structure of sodium-borophosphate glasses, which is partly based on NMR measurements, gives a basis for the explanation of the composition dependence of the few properties that have been described in the literature up to the present time.

6.4. Experimental results and discussion

6.4.1. *Introduction*

The radiation-induced optical and ESR spectra of borophosphate glasses include absorption bands that originate from colour centres of types that can be induced in borate and phosphate glasses. A survey of the absorption bands of the relevant colour centres in borate and phosphate glasses is given in table XX. It can be seen from the energy values of the optical bands and the g-factors of the ESR bands that rather complex spectra may be expected, with appreciable overlapping effects.

TABLE XX

The occurrence of radiation-induced optical and ESR colour-centre bands in borate glasses of composition $x\,M_{(2)}O.\,(1-x)\,B_2O_3$ and phosphate glasses of composition $x\,M_{(2)}O.\,(1-x)\,PO_{2.5}$ and the structural units involved in the structure and/or formation of the colour centres
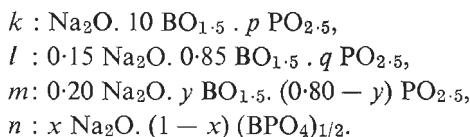
optical band		ESR band	occurrence		structural unit involved
no.	energy(eV)		components	composition	
b_I	1·5	—	Cs_2O, B_2O_3	$x > 0.25$	BO_3 group with a non-bridging oxygen ion (unit of type b)
	1·75	—	Rb_2O, B_2O_3	,,	
	1·95	—	K_2O, B_2O_3	,,	
	2·1	—	BaO or SrO, B_2O_3	,,	
	2·2	—	CaO, B_2O_3	,,	
	2·3	—	Na_2O or MgO, B_2O_3	,,	
II	2·4-2·5	doublet $g = 2.009$ $\Delta g = 0.02$	$MO, PO_{2.5}$ $M_2O, PO_{2.5}$	any x	PO_4 group with a singly bonded non-bridging oxygen ion (unit of type II)
III	3·0	(,,)	$Li_2O, PO_{2.5}$	any x	metal ion acting as a network former (unit of type III)
	3·0	(,,)	BaO, $PO_{2.5}$		
	3·1	(,,)	SrO, $PO_{2.5}$		
	3·2	(,,)	CaO, $PO_{2.5}$		
	3·3	(,,)	MgO, $PO_{2.5}$		
c_I	3·8	singlet $g = 2.014$	MO, B_2O_3 M_2O, B_2O_3	large x	BO_4 group with four bridging oxygen ions and a metal ion as a charge compensator (unit of type c_M' or c_M'')
c_{II}	≈ 5	isotropic quadruplet $g = 2.010$ $\Delta g = 0.008$	id.	medium x	
c_{III}	> 6	anisotropic quadruplet $g = 2.012$ $\Delta g = 0.008$	id.	small x	
IV	≈ 6	—	$MO, PO_{2.5}$ $M_2O, PO_{2.5}$	any x	PO_4 group with a doubly bonded non-bridging oxygen ion (unit of type IV)

In this chapter the colour centres in glasses in the system $Na_2O-BO_{1.5}-PO_{2.5}$ will be discussed first, as a more detailed picture of their glass structure is known. Secondly the influence of the type of metal ions on the properties of the colour centres will be discussed, with reference to glasses of the composition $0.20 \ M_{(2)}O. \ 0.80 \ (BPO_4)_{1/2}$.

6.4.2. *Colour centres in glasses of the system* $Na_2O-BO_{1.5}-PO_{2.5}$

6.4.2.1. Colour-centre formation

These discussions refer to the same series as mentioned in sec. 6.3, namely:

$$k : Na_2O. \ 10 \ BO_{1.5} . \ p \ PO_{2.5},$$
$$l : 0.15 \ Na_2O. \ 0.85 \ BO_{1.5} . \ q \ PO_{2.5},$$
$$m: 0.20 \ Na_2O. \ y \ BO_{1.5}. \ (0.80 - y) \ PO_{2.5},$$
$$n : x \ Na_2O. \ (1 - x) \ (BPO_4)_{1/2}.$$

It may be seen from table XX that the amounts of colour centres of types b_I and II depend on the number of singly bonded non-bridging oxygen ions, which is given by the quantity X'. The amounts of colour centres of the types c_I, c_{II} and c_{III} depend on the number of BO_4 groups of type c_M', which are given by the quantity $_MN_4$.

Now does a unit of type c_P also give rise to the formation of a colour centre, and if so what type of colour centre? If these units react in a way similar to that of units of type c_M' and III, a centre is formed that contains an electron hole on an oxygen ion located between a boron and a phosphorus ion:
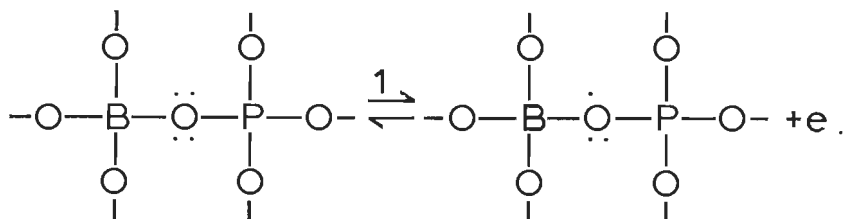
The electron-hole centre formed according to reaction 1 has an excess of positive charge which cannot be compensated as described for units of type c_M' (cf. sec. 3.3.4.3) by departure of the charge compensator to another site in the network, since in the c_P-unit the charge compensator is the tightly bound PO_4 group.

If a stable colour centre is to be obtained, the excess of positive charge must be compensated. A rearrangement of the valency electrons as described in the case of colour centres of type III will lead here to the breaking of the bond between a cation and a singly bonded oxygen ion and the formation of a doubly

bonded non-bridging oxygen ion, as a consequence of the pentavalency of the phosphorus ion (reaction 2). A new centre will then be formed near the spot where the bond was broken. The structure of this centre is not known, but it is clear that it will be able to capture an electron.
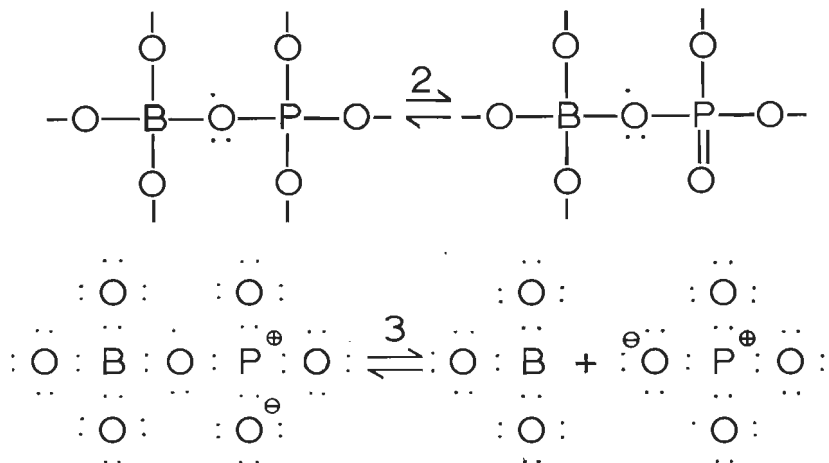
The centre formed by reaction 2 may be converted into a BO_3 group (unit of type a) and a centre of type II by a mechanism described in sec. 5.3.4: an electron of the doubly bonded non-bridging oxygen ion is captured in the electron hole and the bridge between the boron and the phosphorus ion is broken according to reaction 3.

Summarizing, it is seen that the following reactions may occur on irradiation of centres of type c_P.

(1) An oxygen ion between a B and a P ion may lose an electron (reaction 1), which may be followed by the trapping of an electron; i.e. reaction 1 is reversed if the centre is not stabilized in some other way, so that no colour centre is formed and the spectra remain unchanged.

(2) Reaction 1 may be followed by a breaking of a bond between a cation and a singly bonded oxygen ion to neutralize the centre (reaction 2). Such a centre should give rise to an ESR spectrum with a combined hyperfine splitting of a B^{11} and a P^{31} nucleus, which may lead to a spectrum with eight hyperfine bands. The features of the optical bands due to this type of centres cannot be predicted. It will be shown later that the centres formed according to this reaction are not stable and will readily form other centres according to reaction 3.

(3) Reaction 2 may be followed by a breaking of the bond between the bridging oxygen ion with the electron hole and the boron ion (reaction 3). In this case colour centres of type II are formed, which will show bands in the optical and ESR spectra as indicated in table XX.

The quantities X', $_M N_4$ and $_{tot}N_4 = {}_M N_4 + {}_P N_4$ of the four series k, l, m

and n, which determine the numbers of the various colour centres that may be formed upon irradiation, are given in the figures 6.2a to 6.2d.

6.4.2.2. The ESR spectra

Glasses of series k with a low $PO_{2.5}$ concentration show an ESR spectrum similar to that for the corresponding borate glasses (fig. 6.6). On addition of more $PO_{2.5}$ the spectrum becomes more complex, and the doublet with a g-factor of 2·009, assigned in chapter 5 to colour centres of type II, begins to appear. This doublet is more clearly evident in the spectra of glasses of series l (fig. 6.7). It can be concluded from the spectra of these two series that the band remaining
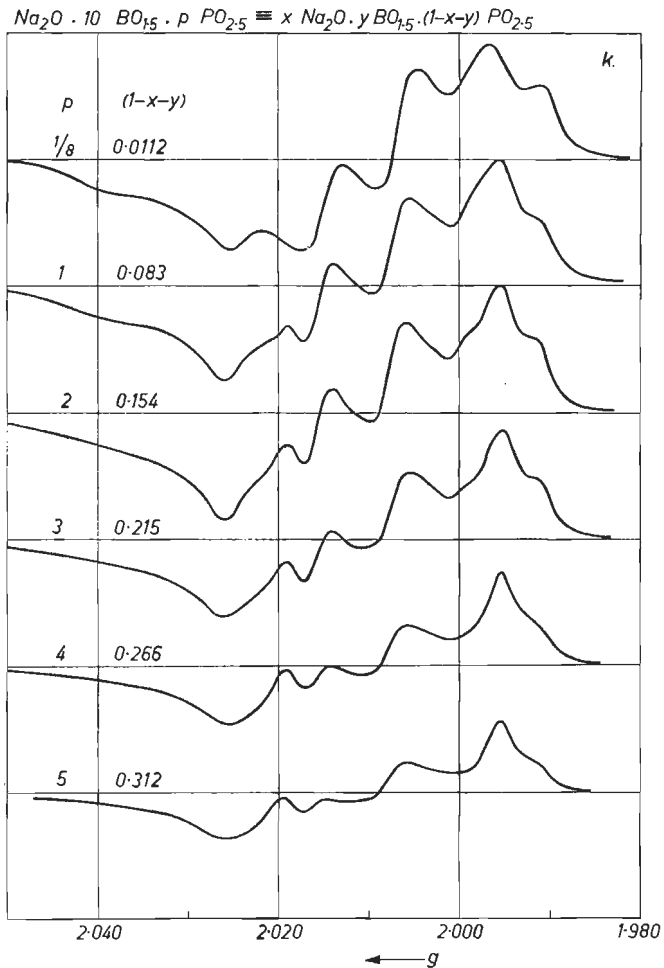

Fig. 6.6. The radiation-induced ESR spectra of glasses of the series Na_2O. 10 $BO_{1.5}$. p $PO_{2.5}$ (line k in fig. 6.1).

$$0.15 \, Na_2O \, . \, 0.85 \, BO_{1.5} \, . \, q \, PO_{2.5} \equiv \, x \, Na_2O \, . \, y \, BO_{1.5} \, . \, (1-x-y) \, PO_{2.5}$$

q	$(1-x-y)$
—	—
0·05	0·048
0·10	0·091
0·20	0·167
0·30	0·231
0·40	0·286
0·50	0·333

2·040   2·020   2·000   1·980

◄———— g
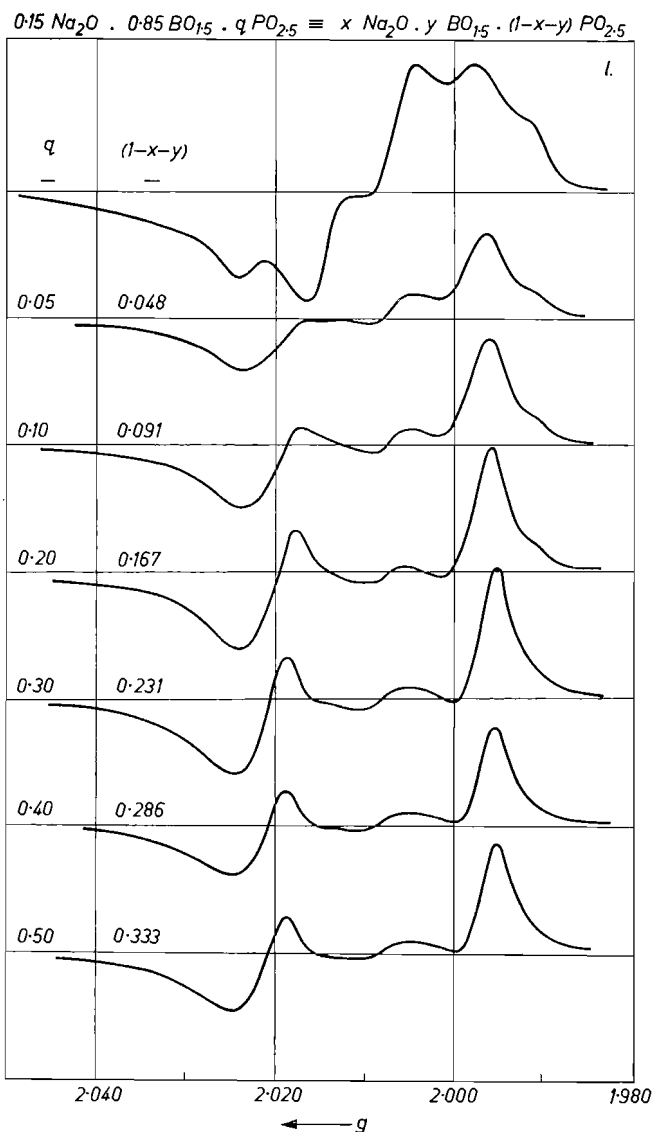
Fig. 6.7. The radiation-induced ESR spectra of glasses of the series 0·15 Na$_2$O. 0·85 BO$_{1\cdot5}$. q PO$_{2\cdot5}$ (line l in fig. 6.1).

visible between the two phosphate bands at higher PO$_{2.5}$ concentrations is due to colour centres of type c (electron hole on a BO$_4$ group), the other bands of the quadruplet due to these centres being masked by the relatively strong phosphate doublet. The doublet due to centres of type II may originate either from units of type II (cf. table XX) or from units of type c_P (cf. sec. 6.4.2.1). Figure 6.2a shows that in glasses of series k the mean number of singly bonded non-bridging oxygen ions X' decreases with increasing PO$_{2.5}$ concentration.

Moreover, X' is very small for these glasses ($\leqslant 0.015$). The number of units of type c_P, given by $_PN_4$, however, increases considerably in the range of $PO_{2.5}$ concentrations above 0.15 to a maximum of $_PN_4 = 0.16$ for about 0.32 mol. $PO_{2.5}$. It may therefore be concluded that the greater part of the colour centres of type II in series k will originate from units of type c_P.

In glasses of series l, X' is about three times larger than in series k. A considerable formation of centres of type II already takes place at compositions where $_PN_4 = 0$, which indicates that in the series l the greater part of the centres of type II originates from units of type II.
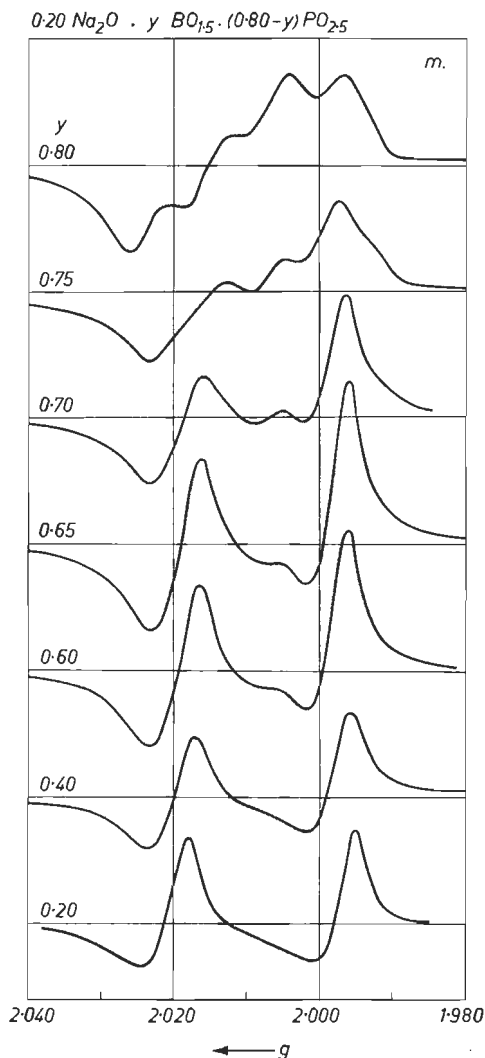

Fig. 6.8. The radiation-induced ESR spectra of glasses of the series 0.20 Na_2O. y $BO_{1.5}$. $(0.80 - y)$ $PO_{2.5}$ (line m in fig. 6.1).

The number of centres of type c, indicated by the band between the doublet giving the number of centres of type II, decreases with respect to the latter as the $PO_{2.5}$ concentration increases. This trend may be explained by the facts that on the one hand the quantity $_MN_4$ decreases monotonically with an increase in the $PO_{2.5}$ concentration and that on the other hand the proportion of singly bonded non-bridging oxygen ions bound to a phosphorus ion will increase with the $PO_{2.5}$ concentration.

In glasses of series m the borate quadruplet decreases rapidly with respect to the phosphate doublet (fig. 6.8). Here the influence of the singly bonded non-bridging oxygen ions bound to a phosphorus ion gives a dominant contribution to the formation of centres of type II, as can be seen from the value of X' (cf. fig. 6.2c). In a glass with 0·60 mol. $PO_{2.5}$ the quadruplet has vanished, which agrees with the disappearance of units of type c_M' at this composition ($_MN_4 = 0$).

In glasses of series n the difference between X' and $_MN_4$ is too large to enable a conclusion about the composition at which the centres of type c disappear (cf. figs 6.2d and 6.9), but the decrease in the relative intensity of the remainder of the borate quadruplet is in accordance with the decrease in $_MN_4$ with respect to X'.
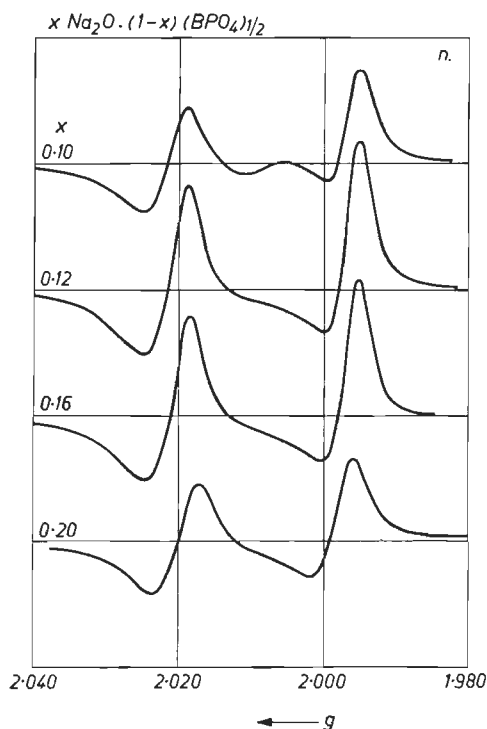

Fig. 6.9. The radiation-induced ESR spectra of glasses of the series x Na$_2$O. $(1 - x)$ (BPO$_4$)$_{1/2}$ (line n in fig. 6.1).

6.4.2.3. The optical spectra

An increase in the $PO_{2.5}$ concentration in glasses of series k gives rise to the formation of two bands (at 2·5 and 3·2 eV) in the radiation-induced optical spectra, which are given as plots of the optical density α (cm^{-1}) versus the energy (in eV) (fig. 6.10). The band at 2·5 eV can be assigned to colour centres of type II. This assignment is confirmed by the induced spectra of series l (fig. 6.11). In the glass without $PO_{2.5}$ a band is found at 2·3 eV, which has been assigned to centres
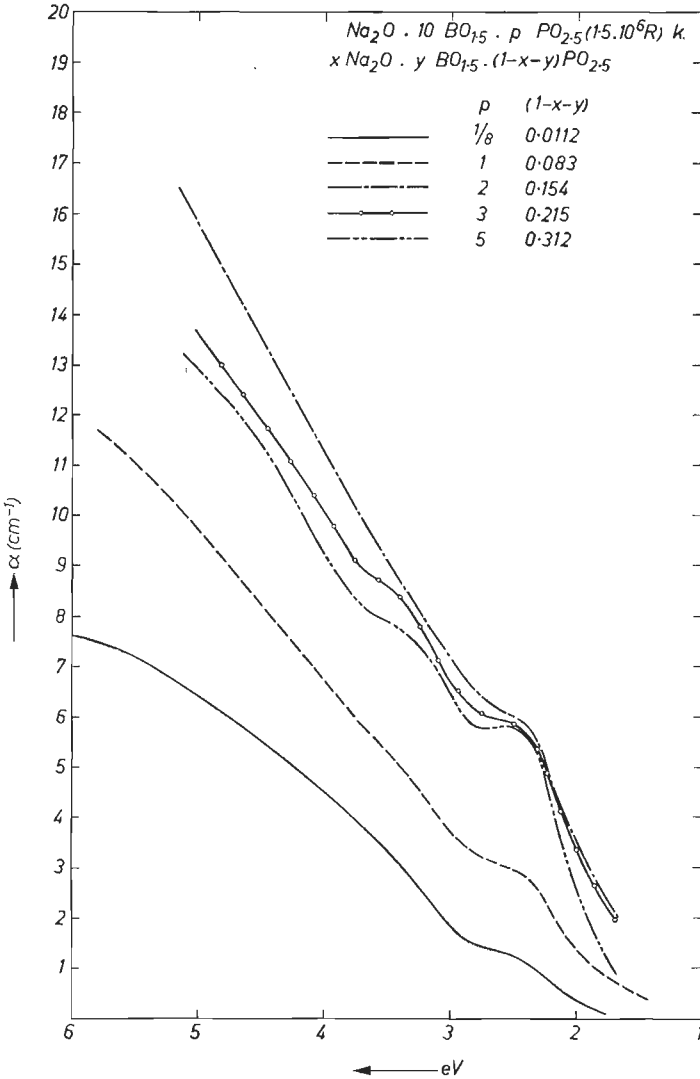

Fig. 6.10. The radiation-induced optical spectra of glasses of the series Na₂O. 10 BO₁.₅. p PO₂.₅ (line k in fig. 6.1).

of type b_I (table XX). Even a small addition of $PO_{2.5}$ causes this band to vanish and the 2·5-eV band to appear. The 2·5-eV band cannot therefore be assigned to centres of type b_I and must be exclusively due to centres of type II.

The vanishing of the 2·3-eV band and the appearance of the 2·5-eV band can be seen even more clearly in the spectra of series m (fig. 6.12), where this effect is accompanied by the simultaneous appearance of the phosphate doublet in
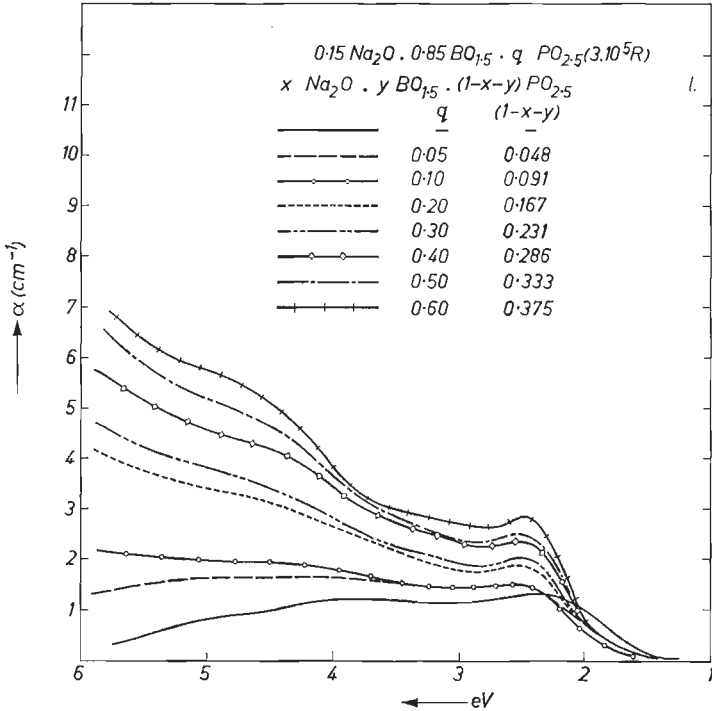

Fig. 6.11. The radiation-induced optical spectra of glasses of the series 0·15 Na_2O. 0·85 $BO_{1.5}$. q $PO_{2.5}$ (line l in fig. 6.1).

the ESR spectra, which is also due to centres of type II. A plot of band energy and intensity against composition in the range of 2 to 3 eV (fig. 6.13) for glasses of series m shows that an addition of 0·1 mol. $PO_{2.5}$ shifts the energy from 2·3 to 2·5 eV, and causes a decrease in the intensity. At higher $PO_{2.5}$ concentrations the energy remains 2·5 eV while the intensity rapidly increases to a constant value up to about 0·50 mol. $PO_{2.5}$. It may be concluded from this effect that the singly bonded non-bridging oxygen ions are preferentially bound to phosphorus ions even if small amounts of $PO_{2.5}$ are present. The intensity curve has been resolved in a contribution of the b_I-centres at low $PO_{2.5}$ concentrations and a contribution of the type-II centres at higher $PO_{2.5}$ concentrations in fig. 6.13.
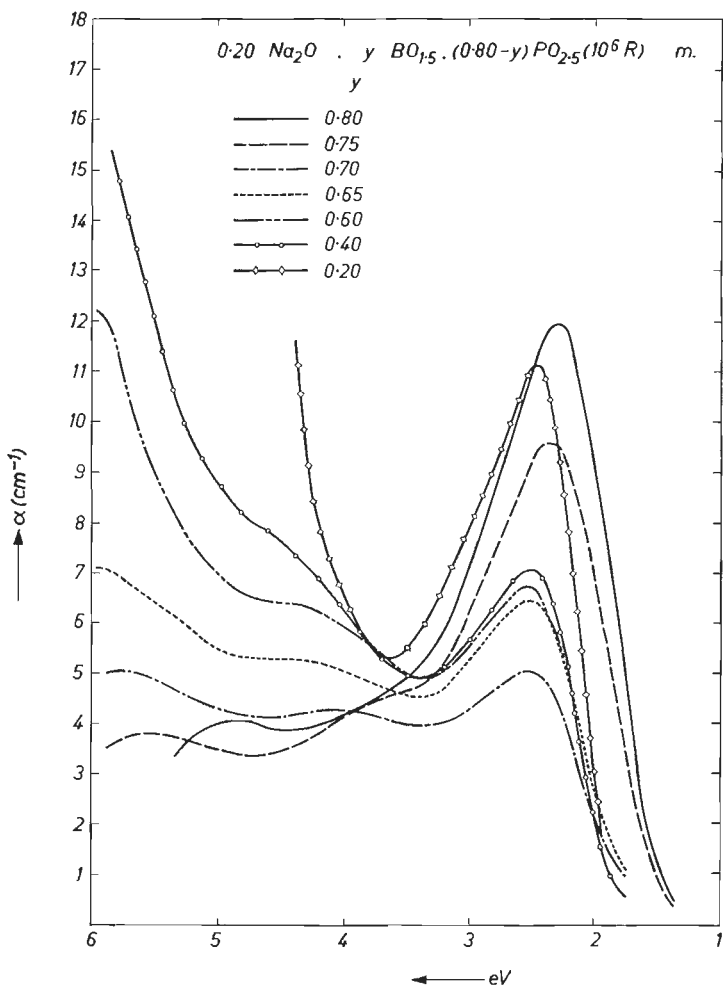
Fig. 6.12. The radiation-induced optical spectra of glasses of the series 0·20 Na₂O. y BO₁·₅ (0·80 − y) PO₂·₅ (line m in fig. 6.1).

A band is observed at about 3·2 eV in the spectra of some glasses of series k (fig. 6.10) and of series n (fig. 6.14). This band is believed to be due to colour centres of type III (cf. table XX). However, it is somewhat confusing that this band is *absent* in all sodium-*phosphate* glasses (cf. sec. 5.3.2.2) but is present in some sodium-*borophosphate* glasses. This apparent contradiction may be understood as follows. The formation of colour centres of type III is favoured by a rigid network. In the case of phosphate glasses this rigidity is achieved by building in metal ions with a high ionic field strength. For example, band III is strong compared with band II in magnesium-phosphate glasses and weak in barium-phosphate glasses. The field strength of sodium ions is too low to permit
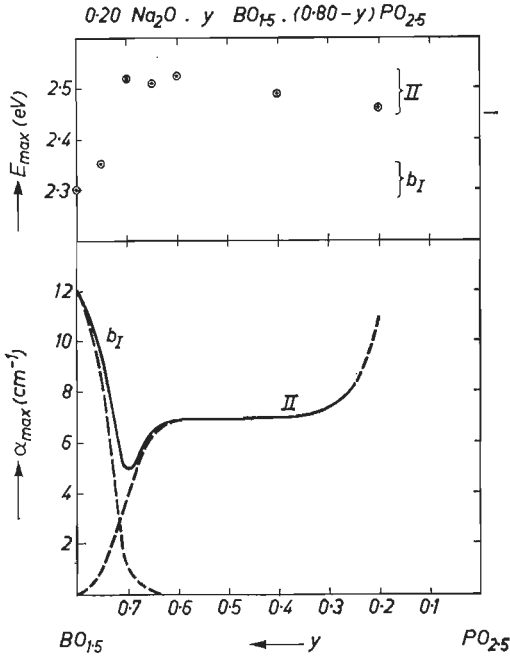
Fig. 6.13. The band energy and the intensity in the range 2-3 eV as a function of the composition in glasses of the series 0·20 Na2O. y BO1·5. (0·80 − y) PO2·5.

the formation of centres of type III, in other words, sodium ions are ionically rather than covalently bound to the singly bonded non-bridging oxygen ions. It is known, however, that O-Na-O bridges do indeed occur in sodium-phosphate glasses (cf. sec. 5.2.4). If the rigidity of the sodium-borophosphate glasses is increased by other bonds than the O-Na-O bridges, a structure is obtained which does not permit these bridges to break on irradiation, and centres of type III may be formed even with sodium ions as constituents. These bonds are found in units of the types c_M' and c_P which may both occur in sodium-borophosphate glasses. If, however, the rigidity of these glasses is decreased by a rise in the number of non-bridging oxygen ions (X'), the amount of centres of type III decreases in favour of the centres of type II. This effect may be seen in fig. 6.15: an increase in the sodium-oxide concentration in glasses of series n gives rise to an increase in X' (cf. fig. 6.2d) which causes band III to decrease and band II to increase.

The intensity of the three bands at 3·8, 5 and 6 eV, which are correlated with centres of the types c_I, c_{II} and c_{III}, respectively, also depends on the degree of coherence of the glass network (cf. sec. 3.3.4.3). A rigid network favours the formation of centres of type c_{III}, whereas a looser network favours the formation of centres of type c_I. This trend may be observed most clearly in glasses of series n (fig. 6.14).
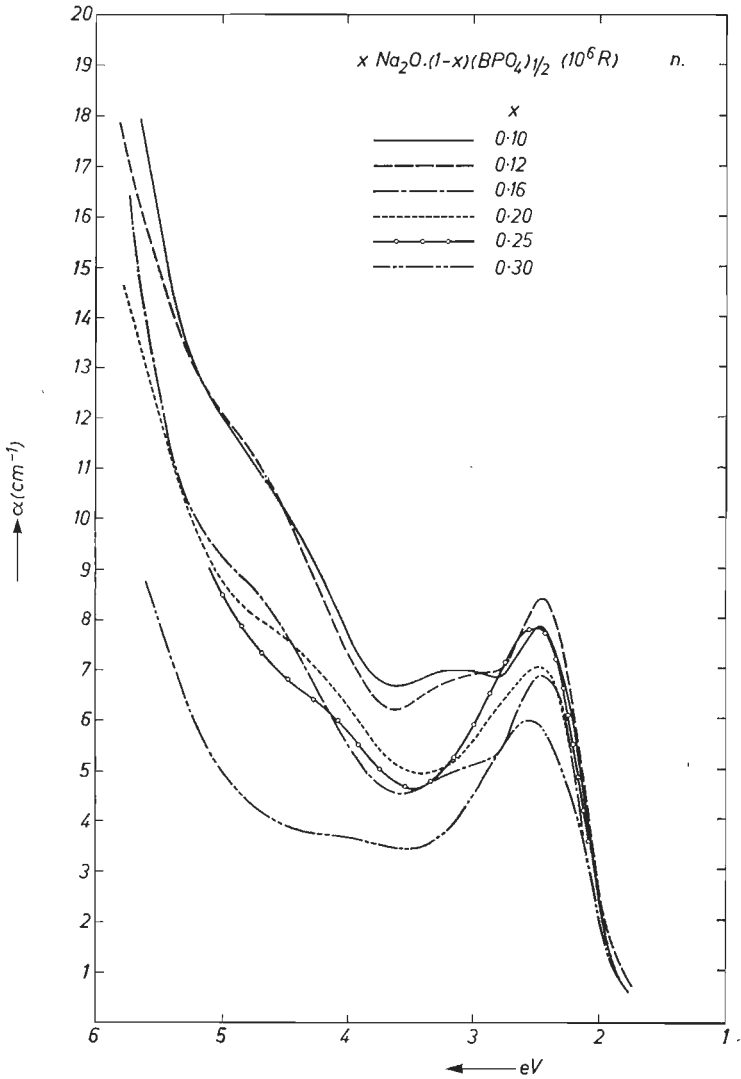
Fig. 6.14. The radiation-induced optical spectra of glasses of the series x Na₂O. $(1 - x)$ (BPO₄)₁/₂ (line n in fig. 6.1).

The quantity $Y = 3 + 2_{tot}N_4 - 2x/(1 - x)$ is correlated with the degree of coherence of the network. The value of $_{tot}N_4$ does not change much in the glass-forming range of this series, but the value of $2x/(1 - x)$ changes from 0·22 for $x = 0·1$ to 0·86 for $x = 0·3$. Hence the degree of coherence decreases considerably with a rise in the sodium-oxide concentration. Parallel with this, the band at about 6 eV decreases, while at $x = 0·30$ the band at 5 eV vanishes, to be replaced by a band at 4 eV. The 6-eV band will not vanish because of the

Fig. 6.15. The intensity of bands II and III as a function of the composition in glasses of the series $x\,Na_2O.\,(1-x)\,(BPO_4)_{1/2}$.

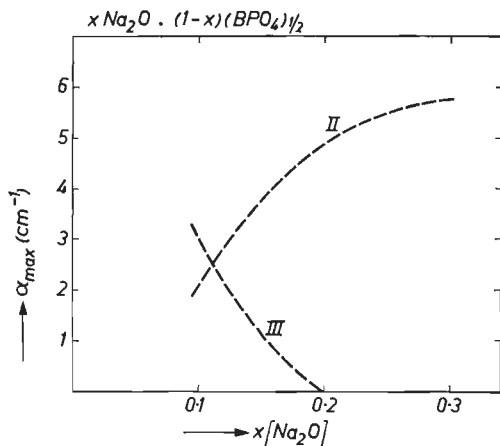absorption at this energy due to phosphate colour centres of type IV, which are present in almost all borophosphate glasses of any composition.

An increase in the degree of coherence also has its effect on the c-bands in glasses of series l (fig. 6.11). This increase in coherence is produced by raising the $PO_{2.5}$ concentration and hence the value of $2x/(1-x)$; it is enhanced above 0·23 mol. $PO_{2.5}$ by the formation of a number of BO_4 groups of type c_P in addition to those of type c_M, which causes a rise in the quantity $_{tot}N_4$. The effect observed is a shift of the c_I-band towards higher energies, which means that the centres become more and more of type c_{II}. Apart from this the 6-eV band increases, which will be mainly due to the formation of centres of type IV.

6.4.2.4. Conclusions

Generally speaking, no types of colour centres are induced in irradiated sodium-borophosphate glasses which are not induced in the borate and phosphate glasses. There are some indications that the specific structural unit c_P, which is believed to be present in borophosphate glasses of certain compositions, may give rise to the formation of an additional number of colour centres of type II.

The hypothesis for the structure of sodium-borophosphate glasses as described in sec. 6.3.3 is supported by the experiments described above:

(1) the centres of type c (electron hole on a BO_4 group) represented by the ESR quadruplet, vanish where $_MN_4 = 0$;

(2) the centres of type III are found in glasses where the degree of coherence is increased by the presence of units of the types c_M' and c_P and is decreased by the presence of units of the types b and II (X'); centres of type III have

not been found in the corresponding phosphate glasses, where units c_M' and c_P are absent;

(3) for glasses with a small value of X' the number of centres of type II and b_I are few in number or even absent; the contribution of units of type c_P to colour centres of type II is mainly small;

(4) centres of type c change from type c_I to c_{II} and further to c_{III} with an increase in the degree of coherence, characterized by the quantity $Y = 3 + 2 \, _{tot}N_4 - 2x/(1-x)$.

Additional information about the part played by singly bonded non-bridging oxygen ions in the structure of sodium-borophosphate glasses is obtained from the colour-centre experiments. The excess of oxygen ions introduced by the sodium oxide, in so far they are not bound to a boron ion as a fourth bridging oxygen ion, will be bound as singly bonded non-bridging oxygen ions to phosphorus ions (unit of type II) rather than boron ions (unit of type b).

6.4.3. *Colour centres in alkali- and alkaline-earth-borophosphate glasses of the composition* $0 \cdot 20 \, M_2O/MO.0 \cdot 80 \, (BPO_4)_{1/2}$

6.4.3.1. Introduction

In this section the influence of the type of metal ions on the formation of the colour centres is discussed. For this purpose a suitable composition should be chosen, so that the various effects of the types of metal ions can be observed rather clearly, and the boron and phosphorus ions have an equal influence. These considerations led to the above-mentioned composition. For the alkali-containing glasses, the values of $_MN_4$ and X' follow from eqs (6.15) and (6.16) and are also given in fig. 6.2d: for $x = 0 \cdot 20$, $_MN_4 = 0 \cdot 14$ and $X' = 0 \cdot 36$. It has been found from NMR measurements that for sodium-containing glasses $_{tot}N_4 = 0 \cdot 30$, and hence $_PN_4 = 0 \cdot 16$.

Equations similar to that for the alkali-containing glasses can be derived for the alkaline-earth-containing glasses using eq. (4.3) instead of eq. (3.13) as a basic relation:

$$_MN_4 = [2x/(1-x)]\{1 + \exp[10 \cdot 85 \, . \, 2x/(2x+y) - 5 \cdot 0]\}^{-1} \tag{6.17}$$

and

$$X' = [2x/(1-x)]\left[1 - \{1 + \exp[10 \cdot 85 \, . \, 2x/(2x+y) - 5 \cdot 0]\}^{-1}\right]. \tag{6.18}$$

For the specific composition discussed here these quantities are $_MN_4 = 0 \cdot 145$ and $X' = 0 \cdot 155$. Obviously the differences between these values for alkali- and alkaline-earth-borophosphate glasses are rather small. Experimental values of $_{tot}N_4$ are only available for the sodium-containing glasses.

6.4.3.2. The alkaline-earth-borophosphate glasses

It has been mentioned above that the excess of oxygen ions introduced by the sodium oxide in sodium-borophosphate glasses will be bound partly as a fourth bridging oxygen ion to a boron ion, forming a unit of type c_M', and partly as a singly bonded non-bridging oxygen ion to either a boron or a phosphorus ion. At the composition in question ($x = 0.20$), practically all these non-bridging oxygen ions are preferentially bound to phosphorus ions. The sodium ions are bound to these oxygen ions ionically rather than covalently, forming units with a type-II character (cf. table XIX). This character of the M-O bond depends on the ionic field strength of the metal ions. A low-field-strength ion will be bound in a more ionic way and a high-field-strength ion in a more covalent way. This means that, although X' remains constant for all the alkaline-earth glasses with $x = 0.20$, the character of the M-O bond shifts from type II to type III with an increase in the field strength, i.e. in the series Ba, Sr, Ca, etc. This change in the character of the M-O bond influences both the optical and the ESR spectra: in the optical spectra the intensity of band II decreases and that of band III increases (fig. 6.16), while in the ESR spectra (fig. 6.17) the phosphate doublet decreases with respect to the borate quadruplet, the intensity of the latter depending on the number of units of type c_M'' which is constant ($_M N_4 = 0.145$). In the beryllium-containing glass all the bands of the quadruplet are observable, while in the spectra of the other glasses only one band of the quadruplet is found between the two phosphate doublet bands; in glasses containing metal ions with a low field strength, the quadruplet is completely absent. No specific bands have been found in the optical spectra between 3.5 and 5.5 eV which may indicate that the c-centres are of the type c_{III}, giving rise to a band at about 6 eV. This conclusion is supported by the anisotropic form of the borate quadruplet in the spectrum of the beryllium glass. As mentioned above, the rigidity of the network is increased when metal ions with a higher field strength are built in the network, and the formation of centres of type c_{III} is then favoured compared to centres of the types c_{II} and c_I (cf. sec. 3.3.4.3).

The number of units of type II and type IV rises simultaneously with a decrease in the ionic field strength. In the optical spectrum this effect is observed as a slight increase of the absorption at about 6 eV, owing to colour centres of type IV as well as the above-mentioned centres of type c_{III}.

6.4.3.3. The alkali-borophosphate glasses

The bands in the optical spectra at 2.5 eV and 3.2 eV can be explained in the same way as for the alkaline-earth-borophosphate glasses (fig. 6.18). The field strength of the lithium ions is apparently high enough to enable the formation of centres of type III. These are not found in the other alkali-containing glasses: the
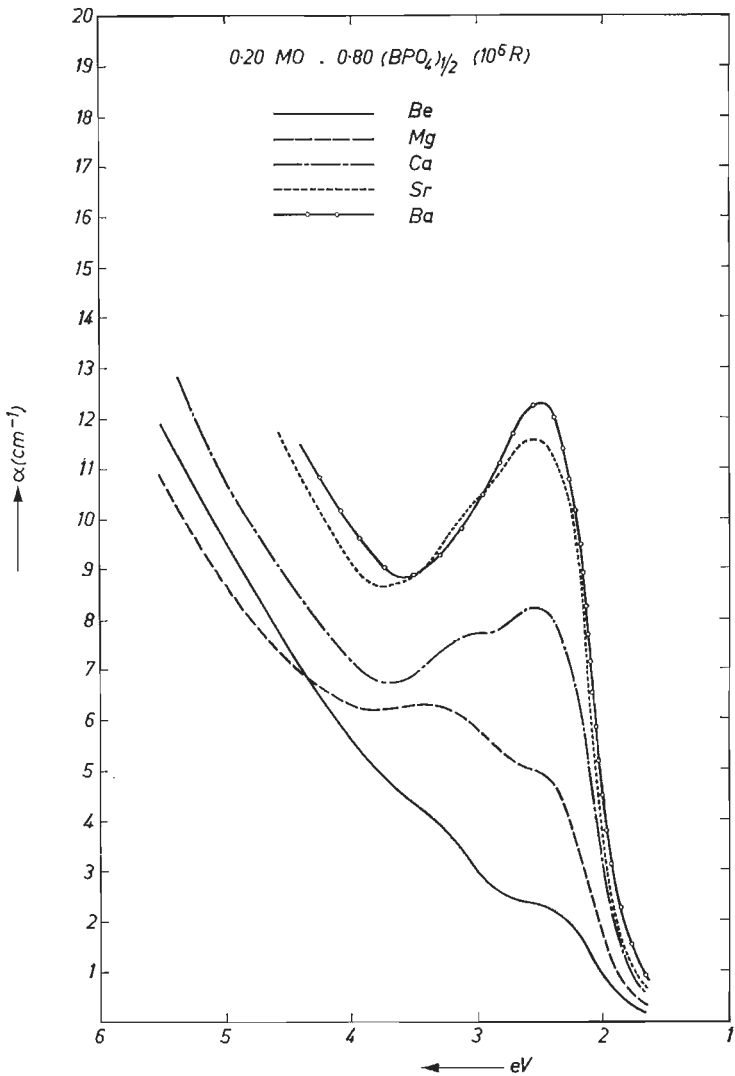
Fig. 6.16. The radiation-induced optical spectra of glasses of the composition 0·20 MO.
0·80 (BPO4)$_{1/2}$.

band at about 3 eV is absent. Band II, on the other hand, increases on the replacement of the lithium ions by sodium ions etc., which indicates that the M-O bond keeps changing towards a more ionic character. This effect is confirmed by the increase in the intensity of the phosphate doublet compared to that of the borate quadruplet in the ESR spectra of the lithium-, sodium- and potassium-borophosphate glasses.

The degree of coherence of the network in the alkali-containing glasses is less than in the alkaline-earth-containing glasses, which is shown by the

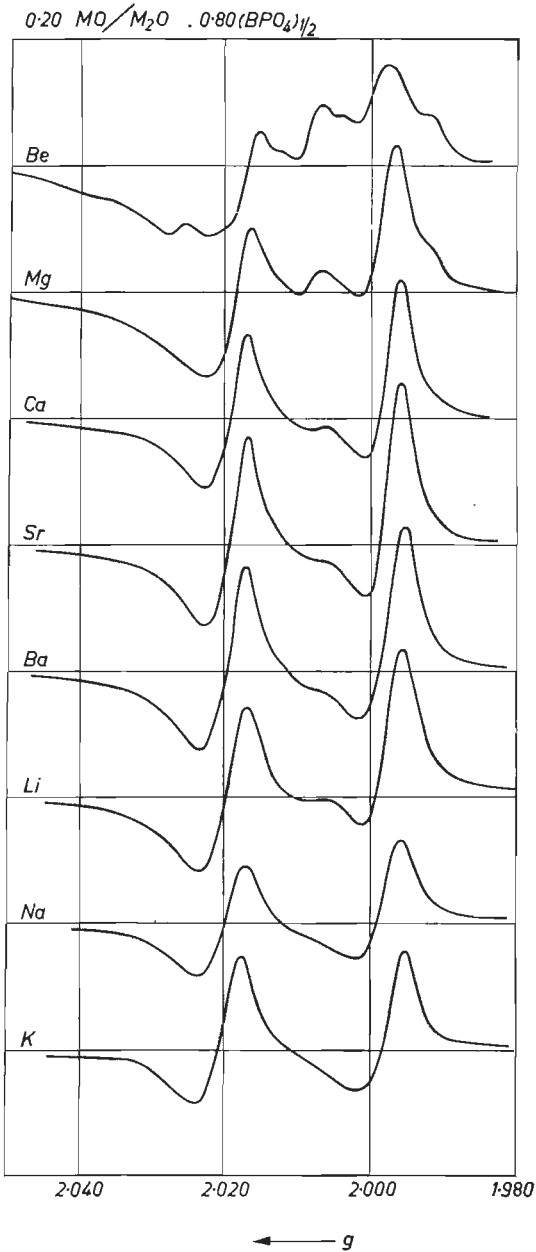Fig. 6.17. The radiation-induced ESR spectra of glasses of the composition $0.20\ M_2O/MO$ $0.80\ (BPO_4)_{1/2}$.

presence of a band at about 5 eV in the lithium glass, which shifts to an energy of about 4 eV in the caesium glass. These bands are due to centres of type c_{II}
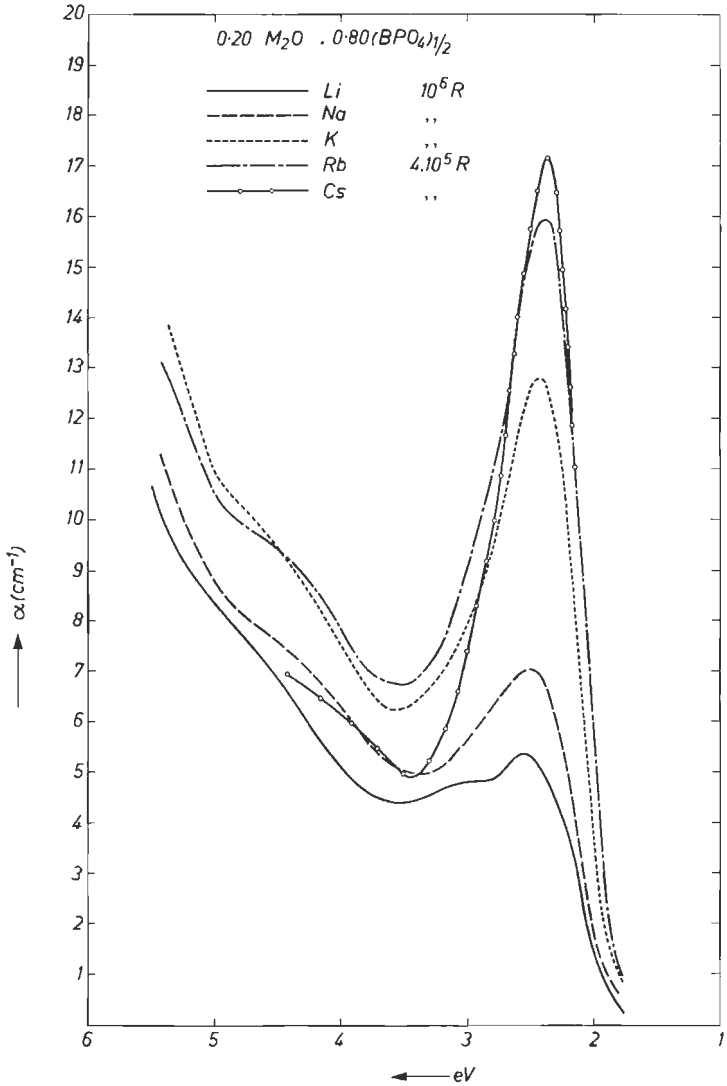
Fig. 6.18. The radiation-induced optical spectra of glasses of the composition 0·20 M₂O. 0·80 (BPO₄)₁/₂.

and c_I, respectively. The change from type c_{II} to c_I is due to the decrease in the degree of coherence in the series Li, Na, K, Rb and Cs.

6.4.3.4. Conclusions

The theory developed for the structure of sodium-borophosphate glasses in sec. 6.3.3 is generally valid for all the alkali-borophosphate glasses. For the

alkaline-earth-containing glasses, this theory has to be modified somewhat, which leads to values of $_MN_4$ and X', which differ only slightly from those for the alkali-containing glasses of the chosen composition 0.20 M_2O/MO. 0.80 $(BPO_4)_{1/2}$. Although the theoretical values of $_MN_4$ and X' are practically constant for any glass of this composition, the colour-centre spectra show appreciable differences. The general cause of these differences is found in the fact that X', which has been regarded as representing the amount of singly bonded non-bridging oxygen ions in the sodium-containing glasses, is no longer a measure of the concentration of this type of oxygen ions in glasses containing metal ions of a higher field strength. The higher field strength changes the character of the structural units from type II to type III. It is known from the discussions of the phosphate glasses that the degree of coherence is increased by a rise in number of structural units of type III. The colour-centre spectra show a number of features due to these changes in the degree of coherence and the number of type II, III and IV units (cf. sec. 5.4):

— the number of colour centres of type II (band at 2.5 eV) decreases and the number of centres of type III rises simultaneously (band at about 3 eV);
— a slight decrease is observed at about 6 eV, as the band here is partly due to centres of type IV;
— the change in the shape of the optical and the ESR spectra indicates that the character of the centres of type c shifts from c_I via c_{II} to c_{III} (cf. sec. 3.3.4.3).

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[5] P. J. Bray and A. H. Silver in J. D. Mackenzie (ed.), Modern aspects of the vitreous state, Butterworths, London, 1960, Vol. I, p. 92.
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Summary

A study is made of the correlation between the structure of borate, phosphate and borophosphate glasses and the colour centres induced in them by high-energy radiation.

It may be concluded from a theoretical discussion of the kinetics of the formation of the colour centres, that in general it is not permitted to discuss the numbers of centres in different glasses in a quantitative way. However, these numbers may be compared in a semi-quantitative way in the case of series of glasses with a gradually changing composition.

The structure of borate, phosphate and borophosphate glasses may be described in terms of structural units. The three types of structural units found in borate glasses consist of

— a boron ion triangularly coordinated by bridging oxygen ions (a),
— a boron ion triangularly coordinated by oxygen ions of which one or more may be non-bridging, with an alkali or an alkaline-earth ion acting as a charge compensator (b),
— a boron ion tetrahedrally coordinated by bridging oxygen ions with an alkali or an alkaline-earth ion acting as a charge compensator $(c_M'$ and c_M'', resp.).

For both the alkali- and the alkaline-earth-borate glasses a set of rules is given which applies to the mutual location of these units.

The structure of the phosphate glasses may be described by four types of structural units, consisting of

— a bridging oxyging ion bonded to two phosphorus ions (I),
— a non-bridging oxygen ion singly bonded to one phosphorus ion with a metal ion acting as a charge compensator (II),
— an oxygen ion covalently bonded to a phosphorus and a metal ion (III),
— a non-bridging oxygen ion doubly bonded to one phosphorus ion (IV).

Apart from the structural units of the borate and phosphate glasses, another structural unit may be found in the borophosphate glasses, consisting of a boron ion in tetrahedral coordination of bridging oxygen ions, the excess of negative charge being compensated by an adjacent group consisting of a phosphorus ion in tetrahedral coordination of singly bonded oxygen ions (c_P).

The radiation-induced colour centres in these glasses have been studied by means of optical-absorption and electron-spin-resonance (ESR) measurements. Models are proposed which may account for the properties of the colour centres. These models are correlated to various structural units that are present in the glasses.

In the borate glasses at least two types of colour centres are found, which may be described as: an electron hole captured on the oxygen ions of a BO_4 group (c_I, c_{II}, c_{III}) and a pair of electrons captured on a non-bridging-oxygen vacancy (b_I). In the phosphate glasses at least three types of colour centres are found, which may be described as: an electron hole captured on a singly bonded non-bridging oxygen ion (II), an electron hole captured on an oxygen ion bonded to a phosphorus and a metal ion (III), and a pair of electrons captured on a doubly bonded non-bridging-oxygen vacancy (IV).

The colour centres found in the borophosphate glasses are of the same nature as those found in the borate and phosphate glasses.

The amounts of the various types of colour centres do not exclusively depend on the number of structural units to which they are correlated; they also depend on the degree of coherence of the network, which can be predicted qualitatively from the hypotheses for the structure of the glasses discussed. The predictions generally agree with the experimentally observed trends in the properties of the colour centres.

Samenvatting

De bestudering van kleurcentra in glasachtige materialen met behulp van electronen-spin-resonantie gecombineerd met optische absorptie metingen kan een beter inzicht verschaffen in de structuur van deze centra en biedt daardoor een mogelijkheid enig inzicht te krijgen in de structuur van deze materialen. De kleurcentra kunnen worden gevormd met behulp van ultraviolet licht, Röntgen- of gammastralen.

Uit een theoretische beschouwing over de vorming van kleurcentra door bestraling blijkt dat in het algemeen een kwantitatieve vergelijking van de aantallen kleurcentra in verschillende glasachtige systemen niet toegestaan is. Indien deze systemen behoren tot een reeks met een systematisch gevarieerde samenstelling, dan is een semi-kwantitatieve vergelijking van de aantallen kleurcentra toelaatbaar.

Het lijkt zinvol de structuur van de boraat-, fosfaat- en borofosfaatglazen te karakteriseren door de "bouwstenen" (structural units) waaruit het netwerk opgebouwd kan worden.

De drie typen bouwstenen van een boraatglas kunnen als volgt worden omschreven:

— een boriumion omringd door drie brugzuurstofionen (a),
— een boriumion omringd door drie zuurstofionen waarvan er één of meer zwevend zijn, met een daarbij behorend alkali- of aardalkaliion als ladingscompensator (b),
— een boriumion omringd door vier brugzuurstofionen met een daarbij behorend alkali- of aardalkaliion als ladingscompensator (c_M' and c_M'', resp.)

Voor de alkaliboraatglazen zijn twee regels opgesteld die de onderlinge rangschikking van de bouwstenen beschrijven. Ook voor de aardalkaliboraatglazen zijn twee regels opgesteld waarvan er een principieel verschilt van die voor de alkaliboraatglazen.

Een fosfaatglas kan opgebouwd gedacht worden uit vier typen bouwstenen, die op de volgende wijze omschreven kunnen worden:

— een brugzuurstofion gebonden aan twee fosforionen (I),
— een zwevend zuurstofion enkel gebonden aan één fosforion met een bijbehorend metaalion als ladingscompensator (II),
— een zuurstofion covalent gebonden aan zowel een fosfor- als een metaalion (III),
— een zwevend zuurstofion dubbel gebonden aan één fosforion (IV).

De borofosfaatglazen kunnen opgebouwd gedacht worden uit de reeds genoemde bouwstenen van de boraat- en fosfaatglazen met als een nieuw type bouwsteen: een boriumion omringd door vier brugzuurstofionen met als

ladingscompensator hieraan gebonden een groep bestaande uit een fosforion omringd door vier enkel gebonden zuurstofionen (c_P).

Het voorkomen en de eigenschappen van de kleurcentra worden verklaard aan de hand van modellen die afgeleid zijn uit de bouwstenen van de glasstructuur.

De modellen van twee typen centra die in boraatglazen zijn aangetoond kunnen worden beschreven als: een electronenpaar ingevangen in een vacature op de plaats van een zwevend zuurstofion (b_I) en een electronengat ingevangen in de zuurstofionen van een BO_4 groep (c_I, c_{II}, c_{III}).

De modellen van drie typen centra die in fosfaatglazen zijn aangetoond, kunnen worden beschreven als: een electronengat ingevangen in een zwevend zuurstofion dat enkel gebonden is aan een fosforion (II), een electronengat ingevangen in een zuurstofion dat zowel aan een fosfor- als een metaalion gebonden is (III) en een electronenpaar ingevangen in een vacature op de plaats van een zwevend zuurstofion dat dubbel gebonden is aan één fosforion (IV).

De kleurcentra in de borofosfaatglazen behoren tot dezelfde typen zoals in de boraat- en fosfaat glazen gevonden zijn.

De frequentie van het voorkomen van de verschillende typen kleurcentra wordt niet uitsluitend bepaald door de aantallen van de verschillende typen bouwstenen, maar wordt mede bepaald door de "mate van samenhang" (degree of coherence) van het netwerk. Deze mate van samenhang kan kwalitatief voorspeld worden uit de hypothesen over de structuur van de onderzochte glasachtige systemen. Deze voorspellingen komen in het algemeen overeen met de waargenomen veranderingen in de eigenschappen van de kleurcentra als een functie van de samenstelling.

Levensloop

Pieter Beekenkamp, geboren op 7 december 1933 te Hoek van Holland, bezocht gedurende de jaren 1946-1951 de V^e gemeentelijke H.B.S. afdeling B, thans Willem de Zwijger H.B.S., te Rotterdam. Hij liet zich in September 1951 inschrijven aan de Technische Hogeschool te Delft. In de periode 1955-1957 vervulde hij zijn militaire dienstplicht. Op 10 september 1959 trad hij in het huwelijk met mej. J. A. Hessels. Op 23 januari 1962 verkreeg hij het diploma van scheikundig ingenieur. Sinds 1 maart 1962 is hij werkzaam in het Natuurkundig Laboratorium van de N.V. Philips' Gloeilampenfabrieken te Eindhoven, onder leiding van Prof. Dr J. M. Stevels.

STELLINGEN

bij het proefschrift van P. Beekenkamp

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21 december 1965

I

De conclusie van Stroud et al. dat de optische absorptiebanden met een maximum in het zichtbare gedeelte van het spectrum van bestraalde silicaat-, boraat- en fosfaatglazen alle veroorzaakt worden door ingevangen electronengaten, is aan ernstige twijfel onderhevig.

J. S. Stroud, J. W. H. Schreurs en R. F. Tucker, Proc. VIIth International Congress on Glass, Brussels 1965, Gordon & Breach, New York-Maison d'Edition s.c., Marcinelle 1965, sec.1.3.3/42.

II

In een glasachtig systeem opgebouwd uit oxiden kunnen boriumionen alleen dan in een vieromringing van zuurstofionen voorkomen, indien dat systeem ionen bevat met een lage veldsterkte zoals gedefinieerd door Dietzel.

Dit proefschrift, Hoofdstuk III, IV en VI.

III

De interpretatie die Eipeltauer en Schaden geven van de temperatuurafhankelijkheid van de viscositeit als functie van de samenstelling van natriumboraatglazen is onjuist.

E. Eipeltauer en K. Schaden, Glastechn. Ber. 35, 505, 1962.

IV

Er dient meer aandacht te worden besteed aan de physische mogelijkheden voor de bestrijding van plantenziekten.

R. Carson, Silent Spring, Hamisch Hamilton Ltd., London 1963.

V

De voorstelling die Bryant et al. geven van de binding van caesiumionen aan een glasoppervlak is onjuist.

P. J. Bryant, C. M. Gosselin en L. H. Taylor, NASA contractor report nr. NASr-63 (06), Washington D. C., July 1964.

VI

De door Ypey gegeven verklaring voor het verschil in de mate van uitloging van een aantal opgegraven glazen voorwerpen is niet waarschijnlijk.

J. Ypey, Ber. Rijksd. Oudheidk. Bodemonderzoek 10-11, 363, 1960-1961.

VII

De door Rau gegeven verklaring van de schaduwopnamen van enkele kwarts-glassoorten is onjuist.

K. Rau, 60 Jahre Quarzglas, 25 Jahre Hochvacuumtechnik, W.C. Heraeus GmbH, Hanau 1961, 77.

VIII

De parameter N, die door Solomin is voorgesteld, biedt geen practische voordelen boven de parameter Y om invertglazen te karakteriseren.

N.V. Solomin, Steklo i Keramika 21, 13, 1964.

IX

Indien de conclusie van Brinkman juist is, dat de dode tijd van een Geiger-Müller telbuis afhankelijk is van de intensiteit, leiden de door hem toegepaste methoden om de dode tijd te bepalen tot onjuiste uitkomsten.

G. A. Brinkman, Radio Chimica Acta 2, 41, 1963.

X

Van de organisatie Bescherming Bevolking kan alleen dan een meer doeltreffend optreden worden verwacht indien de personeelsopbouw van deze organisatie in belangrijke mate gewijzigd wordt.