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ON THE AFTER-GLOW OF SODIUM CHLORIDE AND ITS DECAY

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ABSTRACT The decay of luminescence after-glow excited by X-rays has been investigated in the case of sodium chloride (single crystal), pressed powdered sample of sodium chloride, and sodium chloride with 0·1 % of copper. The effect of annealing the pressed samples at different temperatures as well as of heating the sample during emission has also been studied.

The suitability of various mechanisms and the corresponding decay laws has been discussed. The ideas of trap mechanism as developed by Randall and Wilkins have been utilised to deduce the expected decay law in the present case.

Phosphorescence in the gaseous state can occur only through the presence of an intermediate metastable state; it is therefore understandable that no afterglow of measurable duration occurs in gases as the metastable states in gases generally possess a relatively short duration. After-glows have been observed in denser media, the intensity and duration increase with the viscosity of the medium in general. It is thus reasonable to suppose that there exists an interaction between the electronic transition of the excited particle and the surrounding medium. From general ideas and previous investigations we can state, in short, that (*i*) no after-glow occurs if the medium does not influence the emission process appreciably, *i.e.*, the process occurs entirely within the atom or molecule in a sphere of about 10^{-8} cm. diameter; (*ii*) after-glow occurs when the configuration of the surrounding molecular structure plays a part; for this may change as a result of the absorption process and some time must elapse before the configuration falls back into its former state. After-glow will be accompanied by photo-conductivity if the electron is completely set free as it occurs in certain phosphors. Phosphorescence is therefore generally characterised by photo-conductivity but the reverse is not necessarily true.

A large amount of work has been done about the decay of after-glow of solid phosphors under ultraviolet excitation. The solid solutions of organic dyes were some of the first to be investigated; fluorescein in sugar possesses a fluorescence, originating from an excited state, with a life of 10^{-8} sec and shows an after-glow of a few seconds. The intensity of fluorescence varies with the concentration almost in the same way in solids as in liquid solution which is rather a puzzle because, in solids collisions do not occur as it is supposed in solutions. This indicates that chemical change of some type takes place during preparation. The emission of these phosphors decays according to

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the mono-molecular reaction law $I = I_0 e^{-at}$. Generally speaking, a reduction of temperature increases the time of decay while increase in concentration diminishes the time of decay. Jablonsky (1935) has explained many features of this kind of phosphors by assuming the existence of at least one metastable level lower than the unstable level reached by absorption.

Zinc sulphide is the only phosphor which has been investigated thoroughly by many workers. The decay of luminescene of impurity activated zinc sulphide in general follows a bimolecular law which may be written for simple cases as

$$\frac{1}{\sqrt{I}} = \frac{1}{\sqrt{I_0}}(1 + An_0 t)$$

where A is a constant and n_0 is the number of electrons per unit volume in the conduction band at $t = 0$.

Antonow—Romanowsky (1935) and De Groot (1939) have observed in case of copper activated zinc sulphide that high intensity gives a rapid decay; this also follows from the bimolecular law given above. De Groot has further observed a more rapid decay with shorter wavelength of exciting radiation; according to him this is due to the higher absorbability of shorter wavelength by the medium.

In case of photo-conducting phosphors with stoichiometric excess of either constituent, Mott and Gurney (1940) suggest a different decay law,

$$N_q = An(n+\nu)\ ; \quad n = \frac{\nu}{B\exp.(\nu/kT) - 1}$$

$$B = 1 + \frac{\nu}{n_0}\ .$$

ν = the number of normally unoccupied impurity centres in addition to the ordinary impurity centres.

The slow bimolecular decay may have superposed on it a much more rapid decay in certain cases. The measurements of Strange in case of copper and silver activated phosphors indicate such possibility.

Mott and Gurney (1940) have given the following types of decay for photoconducting impurity activated phosphors :

" 1. For very high emitted intensities an exponential decay with a decay period of the order of fraction of a microsecond, independent of temperature.

2. As the intensity decreases this should change over to a rapid bimolecular decay independent of temperature.

3. For still lower intensities this should change to a slow bimolecular decay with a value of 'A' strongly dependent on temperature.

4. Finally the decay law may change over again to an exponential form dependent on temperature, due to the presence of frozen-in ions. This should only occur when the activating impurity is a stoichiometric excess of one of the constituents."

More recently, Randall and Wilkins (1945) have carried out extensive investigations on the decay curve of phosphors of the recombination type with traps, and allied phenomena; they have also developed formulae to explain the decay curves on the basis of trapping mechanisms. Klasens and Wise (1946) have calculated in a more generalised way the luminescence intensity over the whole period and have shown that the decay becomes bimolecular at high temperatures.

The measurement of decay of luminescence under X-rays has as yet attracted little attention from the experimental workers. Levy and West (1939) in their attempts to improve the suitability of zinc sulphide screens by minimising the after-glow, measured the decay of luminescence of zinc sulphide under X-rays with certain impurities. They found that the addition of very small quantities of nickel greatly reduces the phosphorescence without affecting the fluorescence intensity to a great extent. They also found out the optimum amount. The addition of iron does not affect the intensity much while traces of cobalt greatly reduces the fluorescence intensity. The addition of impurities in case of zinc sulphide also affects the quality of the fluorescence and phosphorescence light.

In the present investigation the nature of the long period decay of phosphorescence after-glow of sodium chloride with and without impurity by X-ray excitation has been studied under different conditions; the various decay laws have been discussed with respect to the present case and the probable mechanism suggested.

EXPERIMENTAL PROCEDURE

The pressed substance in the form of thin plate was excited to luminescence by X-rays coming out from the window of the Hadding tube with copper anticathode run at 35-40 K.V. with 10 m.A The photovoltaic cell connected to a galvanometer, was placed almost in contact with sample on the side opposite to that of the X-ray tube. Two lead covers, both connected to a single lever, were arranged in such a way that when X-rays were incident on one side of the sample, the light and transmitted X-rays from the other side were stopped by one of them and could not reach the photocell; on the other hand, when that cover was raised by pressing the lever, the second lead cover at once intercepted the X-rays incident on the front side of the sample. In this way the light from the back side of the luminescent sample fell on the photocell simultaneously with the cutting off of the incident X-rays. The deflections could be marked off on the scale at regular intervals of time with the help of a stop watch.

The low intensity of luminescence is a great trouble in the measurement of the decay curve. After the lapse of a small interval of time the intensity falls too low to be measured with high accuracy.

that the sodium chloride crystal shows no increase in electrical conductivity under X-rays as is demanded by the zone picture of the crystal, calls for the formulation of other mechanism to explain the phenomena of luminescence in such crystals.

It is now known that the presence of impurity or lattice defects in general causes a number of localised levels between the allowed band of the normal energy spectrum. The electron or the hole may be trapped in any one of these states. This trapping process will lead to a release of a part of the energy which may or may not be in the form of emission. The trapped electrons may be thermally excited to upper bound levels or to the conduction band. In the first case energy may be emitted when the electrons come back to the ground state. In the latter case the electron is free to find out a hole for recombination ; on the other hand, the impurity atom with trapped electrons may bodily move through the lattice encountering another with trapped hole and neutralise it with the emission of a quantum of phosphorescence light.

Since pure sodium chloride does not show any fluorescence under ultraviolet radiation, emission is to be supposed to be taking place in some special position of the lattice, *i.e.*, centres.

Different types of centres are possible in a crystal like sodium chloride :

1 A foreign negative or positive ion may replace one of the negative or positive ions of the regular lattice.

2. An electron may be trapped at a lattice point where a negative ion is missing (F & F′ centres).

3. There are bound levels associated with an ion in the interstitial position of the lattice.

4. At the surface of a crystal crack, where the periodic field is broken off, there exists bound levels in which electrons can exist without being free to move through the crystal.

In the case of the presence of a foreign ion in the lattice (*viz.* KBr KH, KCl Th) the emission is characteristic of the activation and there is no reason why the sample should not be luminescent under ultraviolet radiations. Substances used in the present investigation had little chance of containing any such activator. As regards surface levels, though they are predicted from theoretical consideration, there is no direct experimental evidence of their presence in the crystal. In a normal crystal, at any temperature there are present a number of vacant lattice points. Trapping of electrons into positions, where there are missing negative ions, is possible and actually takes place in alkali halide crystals under suitable circumstances, *viz.*, the crystal in contact with Na or K vapour at high temperature. These are called F centres which give rise to the new absorption bands in the crystals termed as F bands. Tibbs (1939) has calculated the wave function of the ground state for such an electron in case of sodium chloride with some approximation. He finds it to be 3 e.v. below the level of the conduction band and the first excited state. 0.6 e.v. below it. As the ions move into new position of equilibrium after absorption the energy of the electron is raised and there is indirect evidence that the excited state is 0.1 e.v below the conduction band after the absorption process. The filled up F centre is neutral but the wave function of the electron in the centre should extend over a greater volume than that of the replaced negative ion. If now another electron is brought to this centre, the surrounding medium gets polarised pushing adjacent ions into new positions of equilibrium This causes a spherical field which varies as 1/r; a set of stationary states is therefore possible so that it is quite possible that two electrons can be trapped at a vacant lattice point. This type of centres are F′ centres and the F′ band obtained in absorption is due to this mechanism When sodium chloride is exposed to X-rays. the crystal is coloured due to the trapping of electrons in these centres for the same absorption bands are also obtained when the F and F′ centres are created by other means On irradiation therefore at first F and F′ centres are created and then the photoelectrons produced inside the crystal go on exciting and ionising different centres which give rise to luminescence

Now luminescence may be excited in two ways:

1. The emitting centres are directly excited but not ionised

2. The electron from the centres or valence band are raised to the conduction band which will presumably find some centres and be captured; it will in all probability be captured into an excited state causing emission on its return to the ground state.

In case of (1) electrons on absorption of photons are raised to higher states but not freed so that they cannot contribute towards electrical conductivity; if 'n' be the number of electrons in excited states per unit volume at any time 't', then during illumination the rate of decay of electrons in the excited state will be .

$$\frac{dn}{dt} = p - \alpha n$$

which, on solution, yields

$$n - p/\alpha = A e^{-\alpha t}$$

$$At\ t = 0, \quad n = 0,$$

$$\therefore \qquad n = p/\alpha(1 - e^{-\alpha t})$$

α, being a constant for the particular crystal at a given temperature, and p, being the number of electrons raised to higher states per sec. per unit volume.

The intensity of luminescence at any instant is proportional to the number of electrons in the excited state ; hence the intensity grows exponentially to a steady value when an equilibrium is established between the number of electrons raised to excited states and of those coming to the ground state per second.

For decay, $p=0$ and $n=n_0$ at $t=0$, so that $n=n_0e^{-\alpha t}$. Hence $I=I_0e^{-\alpha t}$. Since sodium chloride crystals do not show any increase in conductivity under X-rays, it is natural to infer that luminescence of sodium chloride under X-rays will be of type (1). But for forbidden transition 'α' is of the order of 10^4 sec.$^{-1}$, so that decay law in no case can be slower than $I=\dfrac{I_0}{\exp.(10^4 t)}$; hence the long duration of after-glow as is found in case of sodium chloride cannot be explained by this. Besides, the high temperature dependence of decay rate as has been found in the present case is also difficult of explanation by the simple mechanism, for 'α' should not be much influenced by temperature.

Assuming, on the other hand, that the second type of luminescence occurs in the case of sodium chloride, let us suppose that the crystal contains a number of radiative centres where the electrons are trapped, presumably in the higher states, in order to be able to cause phosphorescence; besides, the crystal may contain a large number of non-radiative trapping centres where the electrons may return to the valence band whence it was originally released without any emission; the last assumption is justified by the fact that the pure crystals do not show any luminescence under ultraviolet radiations.

Let 'm' be the number of radiative centres per unit volume of the crystal and is more or less unaffected by X-ray irradiation. Let 'ν' be the number of non-radiative centres per unit volume also constant for the crystal; if 'n' be the number of electrons at any instant in the conduction band per unit volume the number of vacant holes in the filled band may also be taken as 'n', for the concentration of trapped electrons obtainable by X-ray irradiation of sodium chloride is small even at saturation value. Further when the steady state is reached an equilibrium is established between the number of electrons released to the conduction band per second and those coming back to different positions from the conduction band per second, so that number of electrons trapped in special positions inside the crystal at any instant should have a constant value at a particular temperature of the crystal and inclusion of 'm' and 'ν' will have accounted for those. Hence the number of electrons in the conduction band will decay at the rate given by,

$$\frac{dn}{dt} = -Anm - Bn(n+\nu)$$

so that, $$n=\frac{2a}{N\exp.(2aBt)-1} \qquad \text{where } a=\frac{Am+\nu B}{2B}$$

at $t=0$. $n=n_0$.

$$N=1+\frac{2a}{n_0}$$

After sufficiently long time,

$$n = \frac{Am + \nu B}{n_0 B + Am + \nu B} \cdot n_0 e^{-(Am + \nu B)t}$$

and,

$$I = I_0 e^{-(c + \nu B)t}.$$

Thus the decay is exponential

If n_0 is very large compared to $(Am + \nu B)$,

$$n = \frac{n_0}{1 + n_0 Bt},$$

so that the decay law can be written as

$$I = \frac{I_0}{1 + bt}, \quad \text{where } b = n_0 B.$$

As a matter of fact, luminescence in sodium chloride should consist of fluorescence and phosphorescence ; for the probability of direct excitation of centres is much greater than that of ionisation of the centres. The fluorescence part will decay too quickly to be noticed in the present measurement. Assuming total luminescence intensity to be 'p' times as great as the phosphorescence intensity, the decay law for our purpose should be

$$I = \frac{I_0}{p(1 + bt)} \quad \text{or} \quad \frac{I}{I_0} = \frac{1}{p(1 + bt)}$$

It is easy to see that the experimental curve is widely different from this as much as from the bimolecular law. In order that this may explain the long duration of after-glow, 'b' is necessarily very small ; assuming $\frac{I}{I_0} \sim \frac{1}{20}$ at $t = 1000$ seconds approximately we have,

$$b = \frac{20 - p}{p} \times 10^{-3}, \quad i.e., \; b \sim 10^{-3}.$$

Besides, the absence of any increase in conductivity under X-rays is not clearly understood.

On the other hand, it appears more reasonable to assume that the long after-glow is due to the time the electrons spend in a trap. Mott and Gurney have shown that the probability of capture of electrons in the conduction band by the traps is very large, so that during irradiation by X-rays the electrons are trapped as soon as they are released to the conduction band and the fluorescence is mostly due to the direct excitation of the radiative centres (which may be filled up F and F′ centres caused by X-rays itself or otherwise). In the equilibrium state the crystal contains a fixed number of electrons trapped inside it depending upon the temperature and nature of the crystal. During irradiation a steady state is reached between the supply of electrons to the conduction band and their decrease by trapping mechanism or other transitions; when the illumination is stopped, the release of secondary electrons into the conduction band no longer takes place; the trapped electrons released by thermal energy escape to the conduction band at a rate depending upon the temperature and the depth of the traps; some of these electrons at least meet with radiative centres resulting in emission; proceeding with these ideas, Randall (1945) has explained the long duration decay curve of many phosphors and some other allied phenomena. In a similar way, we can arrive at the decay law expected in the present case.

Let, 'ν' be the number of trapped electrons at any instant per unit volume of the crystal, 'n' be the number of electrons in the conduction band and 'd' the total number of trapping centres, then we have, 'm' having the same meaning as before,

$$\frac{d\nu}{dt} = -A\nu e^{-E/kT} + a(d-\nu)n$$

$$\frac{dn}{dt} = A\nu e^{-E/kT} - a(d-\nu)n - cnm.$$

Assuming that the contribution of retrapping to phosphorescence is small,

$$\frac{d\nu}{dt} = -\nu A e^{-E/kT}$$

and, $$\nu = \nu_0 e^{-A\,\mathrm{exp.}(-E/kT)t}$$

where, $$\nu = \nu_0 \quad \text{at} \quad t = 0.$$

$$\frac{dn}{dt} = A\nu_0 e^{-A\,\mathrm{exp.}(-E/kT)t}, e^{-E/kT} - cnm.$$

Hence, $$n = \frac{u}{cm-\beta} e^{-\beta t} + K e^{-cmt}.$$

where, $$u = A\nu_0 e^{-E/kT}$$

$$\beta = A e^{-E/kT}.$$

$$K = \text{a constant.}$$

$$\text{At} \quad t = 0, \quad n = n_0.$$

$$\therefore \quad n = n_0 \left\{ \left(1 - \frac{u/n_0}{cm-\beta}\right) e^{-cmt} + \frac{u/n_0}{cm-\beta} e^{-\beta t} \right\}.$$

The value of cm is necessarily large so that the first term will be negligible within a short time; the intensity is proportional to 'n'.

Hence $$I = I_0 \frac{u}{n_0 cm} e^{-\beta t}$$

The after-glow period will therefore be highly temperature dependent, for both 'α' and 'β' vary with temperature. In considering the decay we have so far taken into account only one type of trapping centres of depth E; if there be a number of them of different depths,

$$I = I_0 \sum \frac{a}{n_0 cm} \cdot e^{-\beta t} .$$

The effect of retrapping which has been neglected so far is expected to make the decay curve still slower. The long after-glow period, temperature dependence, and the nature of the decay, specially at the late portion of the curve, can thus be satisfactorily accounted for without any difficulty about the absence of photo-conductivity (under X-rays).

The slope of the decay curve for a single crystal of sodium chloride is perceptibly greater than that for the pressed powder samples. The dependence of the slope of decay curve on the particle size of the phosphor (zinc sulphide) was noticed by Antonow Romanowsky ; he found that for powders with grain size of the order of 50μ, the slope is almost double of that for particle size of the order of 10μ. In the present case the particle size was not so small; single crystal used was a colourless transparent sodium chloride crystal (1 cm × 1 cm × 5 mm. approximately) and the powdered sample consisted of particles of average size 10^{-2} cm. It has been further observed in the present investigation that the samples need be pressed into sheets before they exhibit this longer afterglow. This way of preparing samples entails generation of intense local heating followed by cooling producing internal cracks and strain; these will all go to produce a larger number of trapping centres of different depths, which are probably deeper than those present in an unstrained single crystal. These traps will therefore lose their electrons less readily than the other and the decay of after-glow will be thereby slowed down. The inclusion of copper ions in the lattice is also found to be unimportant. This only shows that the copper ions do not play any important role in the mechanism of luminescence; they probably produce local strains in the crystal causing new trapping centres which may account for the comparatively slower decay in the case of NaCl + Cu phosphors.

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