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J. W. Allen and G. L. Pearson

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ABSTRACT

The deep-lying energy levels produced by transition metal impurities in semiconductors are of considerable technological importance. Hitherto they have been treated by empirical means. In this report the application of crystal field theory to the impurity problem is considered and it is shown that we can now begin to understand the behavior of the $3d^n$ impurities in atomic rather than phenomenological terms.

To begin with, some definitions concerning energy levels in a multi-electron impurity are laid down, since different authors have different usages. Next, for the benefit of semiconductor scientists who are unfamiliar with the details of atomic structure and crystal field theory, a survey of these topics is given. The aim is to introduce the concepts and the notation, rather than to give full derivations of standard results.

The final sections of the report deal with applications of the method. By using optical absorption into excited states of the d-shell, together with the usual methods of investigation of semiconductors or phosphors, it is possible to establish the electronic configuration of the impurity. Investigations of transition metals in II-VI and III-V compounds illustrate the sort of result obtained. One simple application is the interpretation of luminescent transitions in such centers. Once the electronic configurations have been established, one can calculate the energy levels. As examples, published data on ZnS and GaAs are interpreted, and the energy levels of some impurities not yet investigated are predicted. Other properties may also be determined, and as an example a calculation of the photo-ionization spectrum is outlined.

In order to show the present state of the field, several tables of results are included. Although some of the material is taken from the literature, much of it is hitherto unpublished and was obtained during the course of work on NASA Grant NsG-555.

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A, B, C	Racah parameters for d^n configurations
E^0, E^1, E^2, E^3	Racah parameters for f^n configurations
F^k, F_k, G^k, G_k	Slater-Condon parameters
A_1, A_2, E, T_1, T_2	irreducible representations of the tetrahedral group
$\underset{\sim}{L}^2, L$	operator and quantum number of orbital angular momentum
$\underset{\sim}{L}_z, M_L$	operator and quantum number of z-component of orbital angular momentum
$\underset{\sim}{S}^2, S$	operator and quantum number of spin
$\underset{\sim}{S}_z, M_s$	operator and quantum number of z-component of spin
$\underset{\sim}{J}^2, J$	operator and quantum number of total angular momentum
$\underset{\sim}{J}_z, J_z$	operator and quantum number of z-component of total angular momentum
ℓ, m_ℓ, s, m_s	single electron quantum numbers corresponding to L, M_L, S, M_s
s, p, d, f	single particle orbitals with $\ell = 0, 1, 2, 3$
S, P, D, F	atomic orbitals with $L = 0, 1, 2, 3$
e	electronic charge
$E(\psi)$	energy of the state ψ
$\mathcal{H}$	Hamiltonian operator
$\hbar$	Planck's constant
m	electronic mass
n	principal quantum number
r_{ij}	distance between particles i and j
$R_{n\ell}(r)$	radial function
$U(r)$	potential energy function
$Y_\ell^{m_\ell}(\theta, \varphi)$	spherical harmonic
Z	nuclear charge

β	Racah parameter reduction factor
Γ_i	a general irreducible representation
Δ	crystal field parameter
λ	spin-orbit parameter
ψ	a wave-function
$\xi(r)$	the spin-orbit coupling function
φ_1	constant term in ionization energy
η	linear term in ionization energy

I. INTRODUCTION

Semiconductors owe their importance largely to the fact that their properties can be changed drastically by small concentrations of impurities. The behavior of some impurities can be understood in terms of Bethe's model, in which an electron or hole is bound to the impurity in a hydrogen-like orbit. The behavior of other impurities is not understood. For instance, we have no way of predicting the properties of cadmium telluride doped with molybdenum, or of molybdenum telluride doped with cadmium. As a result, the study of photoconductivity, luminescence, carrier lifetime or any other property depending on deep-lying levels has had to proceed in an empirical fashion. It would be desirable to have a theory which could provide a guide.

A certain class of impurities, namely the transition and rare earth metals, can be treated by crystal field theory, and it is the aim of this report to show what can be done in this way, and how much has been done already. Although crystal field theory has been in existence for many years, it has only recently been applied to semiconductor problems. We have therefore thought it worth while to give an outline of the necessary basic ideas, as an introduction to those workers in the semiconductor field who might be unfamiliar with the subject. The later sections of the report deal with actual applications to semiconductor studies. In these sections some of the data and some of the ideas are collected from the literature, but a substantial amount of new work is included, most of which was performed under NASA Grant NsG-555.

It is hoped that the report will demonstrate the fruitfulness of the crystal field approach and will encourage further work in the area.

II. NOMENCLATURE OF IMPURITY STATES

A complete description of the electronic state of an impurity would require a listing of all the filled orbitals, in general an impossible task. It is, therefore, necessary to use labels which give sufficient information to identify a state, and which by convention imply further information. For instance, Mn d^5 denotes a manganese atom with five electrons in 3d-orbitals. The inner shells will have the same configurations as a free atom. This particular label gives no information concerning filled outer orbitals which may take part in bonding, but for some purposes, e.g. in describing optical absorption spectra, this may not be necessary.

Confusion arises when the label used is the charge state of the impurity, since two different conventions are in use. Some solids, e.g. NaCl, may be treated to good approximation as an assembly of ions, Na^+ and Cl^-. Thallium as an impurity will have an electronic configuration similar to that of a free thallium ion, and so it is natural to denote it Tl^+. This usage has been extended to other solids in which some co-valent bonding occurs. For instance, if manganese is a substitutional impurity in zinc selenide it will contribute its outer two s-electrons to bonding orbitals. If the crystal were ionic, one would denote the impurity as Mn^{2+}. The crystal is in fact quite a long way from being purely ionic, but some characteristics of the Mn^{2+} ion are retained in the crystal as, for example, the existence of a d^5 configuration. If one is examining these particular characteristics, for example, if one is observing electron spin resonance in the d^5 configuration, then it is natural to use the label Mn^{2+}, although it is always necessary to bear in mind the existence of bonding electron orbitals with appreciable magnitudes at the manganese atom which are not implied by the label. On the other hand, if one is considering such things as bonding energies, which depend strongly on the bonding orbitals, then the label Mn^{2+} can be misleading. As the crystal becomes more covalent, a description of an impurity in terms of an ion becomes less reasonable. For instance, an ionic notation for a shallow acceptor in germanium would be very artificial.

Semiconductor physicists working with covalent materials have adopted an alternative approach, in which the charge attributed to an impurity is just the extra charge introduced locally. Substitutional arsenic in germanium has one extra nuclear charge and one extra electron to balance it. There is, therefore, no net extra charge and the impurity is labelled As°. The extra electron is weakly bound and at room temperature will be thermally ionized: in this case the arsenic is As^{+}. The charge state defined in this way has an operational significance, since at a distance the impurity will introduce an electrostatic potential equal to that introduced by a point charge of corresponding magnitude. Conduction electrons or holes will be scattered by this potential, and the strength of the scattering gives the impurity charge directly.

Both notations are in general use, and it is often left to the reader to guess what is meant. So in gallium arsenide, Fe^{2+} and S^{-} may both refer to impurities which have accepted an electron and have a negative charge relative to the rest of the crystal.

Another label sometimes used is the valency, which is the number of electrons from the impurity mainly used in bonding. Divalent manganese will contribute two electrons to bonding orbitals and will retain the d^5 configuration. This label is less confusing than the ionic one, since it does not carry the implication that the bonding orbitals have small magnitude at the manganese atom.

In this report all these notations will be used, but an attempt will be made to indicate the convention to be followed in each case.

III. ENERGY LEVEL DIAGRAMS

It is common practice to refer to the energy of an impurity level with respect to the conduction or valence band of a semiconductor, and to illustrate this by means of diagrams of the type of Fig. 1. In order to use such descriptions unambiguously, it is necessary to state exactly what is meant. This is merely a matter of convention, but different conventions are in use and often energy level diagrams are given without a statement of their meaning, with the result that considerable confusion exists. A detailed analysis of the situation may clarify matters.

FIG. 1. CONVENTIONAL REPRESENTATION OF AN IMPURITY LEVEL.

The conduction band of a semiconductor is usually thought of as a set of one-electron energy levels, in the sense that if an electron is in one of the levels its energy will be independent of what other levels are occupied. Coulomb repulsion and similar interactions between two electrons in the conduction band are regarded as small perturbations, not affecting the main properties of the band. A single level of a hydrogen-like donor can be treated in the same way. If an electron is in the ground state of the donor (vide Fig. 2) then its energy will, to first order, be independent of the occupancies of the conduction band levels. The impurity ionization energy, represented in the diagram by the distance from the ground state to the

FIG. 2. EXCITED STATES OF A HYDROGEN-LIKE DONOR (SCHEMATIC).

conduction band edge, is just the energy required to remove an electron from the ground state of the impurity and place it in the lowest conduction band level. There will be a series of excited states, shown schematically in Fig. 2, and each can be occupied by just one electron, with the important proviso that on each impurity atom only one of the levels may be occupied at any one time.

Similarly, the valence band is thought of as being a set of one-hole energy levels, and the levels of a hydrogen-like acceptor, shown schematically in Fig. 3, will be one-hole levels. By convention, electron energies increase upwards, hole energies increase downwards.
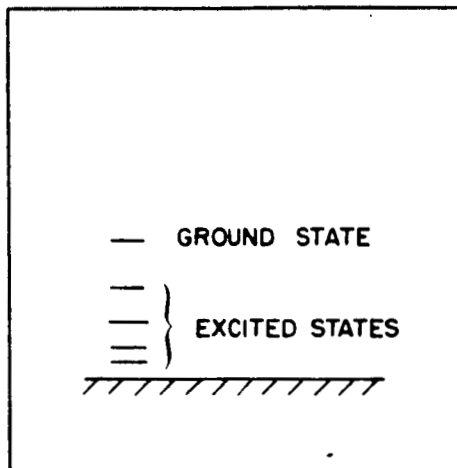
FIG. 3. EXCITED STATES OF A HYDROGEN-LIKE ACCEPTOR (SCHEMATIC).

Most impurities cannot be described in such a simple way. In general the impurity will contain many strongly interacting electrons, whose energies cannot be separated into one-electron terms. In addition, there is an ambiguity between hole and electron energies. To circumvent these difficulties, we formally define the position of a level with respect to the conduction band as being the energy required to remove an electron from the impurity and place it in the lowest level of the conduction band far from the impurity. Defined in this way the level is a characteristic not of one impurity state, but of two, namely the state with n electrons and the one with n-1 electrons, and should be labelled accordingly as $E(n,n-1)$. The relation between states and levels can then be shown diagrammatically as in Fig. 4. One electron can be put into each level in turn, starting with the lowest one. In this way many of the features of a one-electron description can be preserved.

The label $E(n,n-1)$ is hardly ever used in practice, except in theoretical work.[*] This is because it requires three pieces of information,

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[*] A short-hand form, $E(n- 1/2)$, has been suggested.[1]

namely the impurity states before and after the transition, and the energy, and one rarely knows all three. Unless there is some clear advantage to working in terms of holes, as in hydrogen-like or helium-like acceptors, we adopt the convention that the level $E(n,n-1)$ is to be associated with the impurity state with n electrons. Then the energy level of an impurity in a certain state is given by the energy required to remove an electron from the impurity and place it at the bottom of the conduction band far away.

This convention is quite arbitrary, and also inconvenient because it loses symmetry between electrons and holes. It is used here simply because experimental results are often expressed in this way. However, in reading original papers on the subject one must remember that this particular convention is not universally followed, and sometimes $E(n,n-1)$ is attributed to the state n-1. Unfortunately in many cases an energy level will be attributed to a particular state with no indication as to whether this is the state when the level is occupied or empty.

An advantage of the convention adopted here is that it makes it possible to show excited states on the same diagram as the ionization transitions. The excited states correspond to various arrangements of the electrons on an impurity, without changing their number, and so are characteristic of the impurity charge state. Figure 5 shows a possible energy level diagram. In transition a an electron is removed from the valence band and placed on the impurity, which has n-1 electrons before the transition and n after. In transition b an electron is removed from the impurity and is placed in the conduction band, the impurity having n electrons before and n-1 after. In transition c the impurity goes to an excited state but the number of electrons remains constant at n-1.

FIG. 4. RELATION BETWEEN CHARGE STATES AND ENERGY LEVELS.

An alternative form of diagram which has some advantage, especially in considering recombination kinetics in photoconductivity and luminescence, is shown in Fig. 6. Here changes in charge state are denoted by diagonal
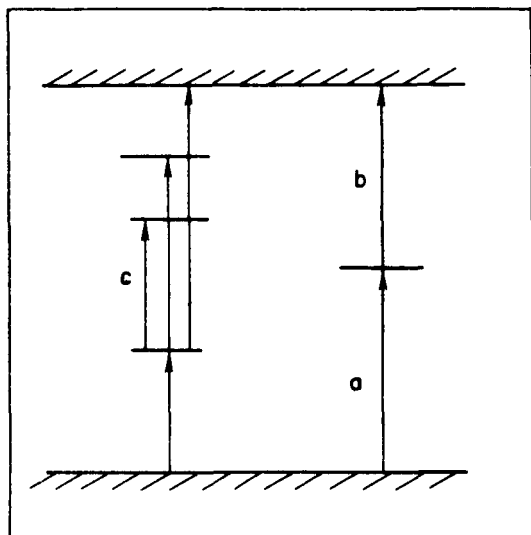
FIG. 5.   ENERGY LEVELS OF A
MULTIPLY-CHARGED IMPURITY.
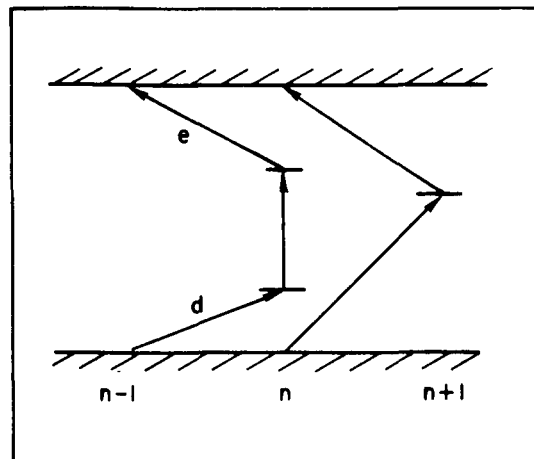
FIG. 6.   DIAGONAL DIAGRAM FOR
IMPURITY TRANSITIONS.

lines, transitions to an excited state by vertical lines. Transition d begins with n-1 electrons on the impurity and ends with n together with a valence band hole. Transition e begins with the impurity in an excited state with n electrons and ends in a ground state with n-1 electrons, together with a conduction band electron. Rather more complicated diagrams are possible if the ionization starts and ends with excited states.

Reverting to Fig. 4, there is a ladder of energy levels which can be continued downwards until all electrons are stripped from the impurity nucleus, and which can be continued upwards indefinitely. In semiconductors one is largely concerned with those levels which fall within or close to the energy gap of the host substance. If the neutral state (i.e. the charge state in which the impurity introduces no extra charge into the lattice) has n electrons, then the levels $E(n+1,n)$ and higher will be acceptors, and $E(n,n-1)$ and lower will be donors.

If the highest filled level of the ladder lies within the conduction band then auto-ionization will occur, i.e. an electron will go from the impurity into a conduction band state and then will be scattered to near the bottom of the conduction band. These processes have short lifetimes.

Similarly if the lowest empty level lies within the valence band it will rapidly be filled. An important result can be deduced. If an impurity has more than one stable charge state then all but one of the corresponding levels must lie within the energy gap. Figure 7 illustrates this rule. (We use the convention that $E(n, n-1)$ is associated with impurity state n and is written E_n.) Level E_n must be full and level E_{n+3} must be empty in the stable state, while E_{n+1} and E_{n+2} may be full or empty. It will then be possible to observe, under suitable circumstances, three charge states, n, n+1 and n+2. Iron in ZnS has been observed as d^5 and d^7 by spin resonance and as d^6 by optical absorption, so it must have at least two levels in the energy gap. In semiconductors with very narrow conduction or valence bands this conclusion may be modified, since it is possible in principle to have a filled level above the top of the conduction band with a long, although not infinite, lifetime.
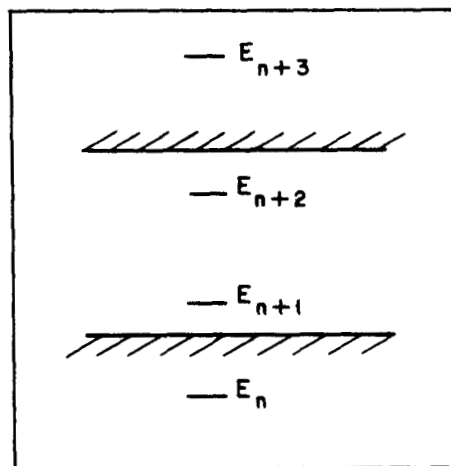
FIG. 7. AN ENERGY-LEVEL LADDER.

In conclusion, energy level diagrams are useful tools but in any given context their meaning must be clearly defined if they are to communicate information effectively.

IV. SUBSTITUTIONAL TRANSITION METAL IMPURITIES

The general theoretical problem of determining the electron wave-functions and energies for an impurity in a crystal is a difficult one, because a large number of electrons and a much larger number of electron-electron interactions are involved. To make progress it is necessary to choose simple systems. The hydrogen-like model has been successful because it treats just one electron moving in the periodic potential of the host crystal, to which is added the Coulomb potential of a point charge, representing the impurity nucleus. The impurity wave-function is expanded in terms of the wave-functions of the crystal in the vicinity of the energy gap. Information concerning these functions, obtained from electrical or optical measurements on the pure crystal, can then be used directly in describing the impurity. The power of the method resides in the fact that no specific information is required about the impurity itself, other than its charge.

At the other extreme, there are impurities which retain in the solid many of the properties which they exhibit as a free ion. A great deal is known concerning the electronic states of free ions, as exemplified by the treatise of Condon and Shortley,[2] and one may hope to use this information with a minimum of modification. Such an approach should be particularly applicable to the transition metals of the $3d^n$ series and the $4f^n$ rare earths, since in these cases there is an incomplete electronic shell which is shielded by the outer electrons, so external influences are comparatively small. In the rare earths the $4f^n$ shell is so well shielded that the energies of transitions within the shell differ by only a few percent between a free ion and an impurity in a crystal. The $3d^n$ shell is less well shielded and the binding energies of electrons in the shell are comparable with those of the outer, bonding electrons. It is this which makes $3d^n$ transition metals so important in the semiconductor field-- electrons can be exchanged between the impurity and the crystal with small energies, so these impurities have levels lying within the energy gap. As examples, copper-doped CdS can be a sensitive photoconductor. Copper in ZnS is a luminescent center, while cobalt and iron quench visible

luminescence. Chromium-doped GaAs has high resistivity and is useful as an insulating substrate.

We shall consider the particular case of a $3d^n$ impurity on a substitutional site in a crystal with zinc-blende structure, so that the local environment is tetrahedral, with four nearest neighbors. (The conclusions reached for the zinc-blende structure will apply with only small perturbation to the wurtzite structure, since this has nearly tetrahedral local symmetry.) We choose this case because of its simplicity and because there are experimental data with which to compare theory, but the method is of much wider applicability.

In a tractable model the electron orbitals must be divided into groups such that interactions between the groups can be treated as second order effects. For the $3d^n$ impurities we make a division into inner core, bonding and d-orbitals. The inner core electrons play no part in semiconductor phenomena except insofar as they contribute to the potential for the outer electrons. The bonding orbitals are considered to be merged in the valence band of the host crystal. The d-orbitals are similar to those in the free ion.

For illustration we take cobalt, which as a neutral atom has the configuration $3d^7 4s^2$ with an argon-like core. Zinc in ZnSe contributes two electrons to bonding, the bonding orbitals constituting the valence band. When a cobalt atom replaces a zinc atom and is in the neutral state, it will likewise contribute two outer electrons to the valence band and will retain a $3d^7$ shell.

Next we take cobalt in GaP, in which it acts as an acceptor. When the cobalt has accepted an electron it can contribute three electrons to binding, as does the gallium it replaces, and will still have a $3d^7$ configuration. In the neutral state two possibilities occur. The cobalt may still contribute three electrons to bonding and have a $3d^6$ configuration. Alternatively the d-electrons may be so tightly bound that instead a hole is left in the bonding orbitals, and cobalt will act as a hydrogen-like acceptor, as would be expected for a divalent atom in a III-V compound. (Coupling between the hole and the d-shell can give a large core correction to the energy.) Which of these alternatives occurs in practice must be determined either by experiment, or by calculating the energies

of the two configurations and finding which lies lowest, a task not computationally possible at the present time. (Incidentally, whichever configuration has the lowest energy, the other will be a possible excited state of the system.) Of course, neither description will be exact and a better approximation would be to take a mixture of the two states, represented schematically by

$$\alpha\psi(d^6) + \beta\psi(d^7, p_v)$$

where p_v denotes a hole associated with the valence band.

The justification for the model lies in the experimental observation that, for many impurities of the type considered, spin resonance and optical absorption data can often be interpreted by considering the impurity to have an incomplete d-shell, strongly localized. All other occupied orbitals behave as closed-shell configurations.

At first sight it may appear to be surprising that the bonding electrons do not need specific treatment but may be considered as being in valence band orbitals. Again we may appeal to experimental observation, this time by considering systems in which a d-shell is absent, so all effects are bonding effects. When phosphorus replaces arsenic in GaAs, the number of bonding electrons is unchanged. It is found that phosphorus does not introduce any electronic states within the energy gap, nor does it cause any extra scattering of electrons, so the presence of phosphorus as an impurity at small concentrations leaves the valence and conduction bands effectively unchanged. In some other similar systems it is found that the impurity can decrease carrier mobility but still not introduce extra levels. In systems with more ionic bonding it is found that similar impurities can produce extra levels within the energy gap as well as contributing to scattering. The situation can be understood in the light of pseudo-potential theory. The kinetic and core potential terms in the Hamiltonian are large but of opposite sign, and nearly cancel each other. As a result the electrons of interest behave as if they moved in a weak potential arising largely from the other outer electrons. The difference of pseudo-potential between phosphorus and arsenic in the example above is so small that the perturbation does not produce bound states or even

any appreciable scattering. Near the nucleus the actual wave-functions will be approximately those in a free phosphorus atom, but at the periphery of the impurity they will join smoothly to the valence band wave-functions. We expect the bonding electrons of our transition metal impurities to behave similarly.

Quantitatively the d-orbitals may be quite different from those of a free ion, but they may still be characterized by their symmetry properties. Crystal field theory, in its various forms, treats this problem. Since there are a number of excellent texts on the subject, in particular those of Ballhausen[3] and Griffith,[4] we shall merely give a brief review for those who are new to the field. In a subsequent section it will be shown how the results of the theory may be used to interpret the properties of impurity states, and some ways of extending the theory to describe impurity levels will be discussed.

V. CRYSTAL FIELD THEORY

A. Introduction

In this section we give a brief account of crystal field theory, originally developed by Bethe.[5] Firstly the free ion is considered, its eigenfunctions are classified by sets of quantum numbers, and its energy levels are found. The host crystal is then treated as a lattice of point charges whose electric field produces a Stark splitting of the impurity levels. Later the adequacy of the approximations introduced and the relation of the point-charge model to more realistic descriptions of the host crystal will be discussed. All of this material may be found in standard texts;[3,4] the purposes of our survey are to indicate the method of approach, to point out the approximations used, and to establish the notation and terminology used in later sections.

B. Free Atoms

To sufficient accuracy, the Hamiltonian for an atom (which may or may not be ionized) containing n electrons is

$$\mathcal{H} = \sum_{i=1}^{n} \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + \xi(r_i)\underset{\sim}{\ell}_i \cdot \underset{\sim}{s}_i \right] + \sum_{i>j}^{n} \frac{e^2}{r_{ij}} , \qquad (1)$$

where Z is the nuclear charge, r_i the position of the i-th electron and r_{ij} the separation of the i-th and j-th electrons. The term in $\underset{\sim}{\ell} \cdot \underset{\sim}{s}$ arises from spin-orbit splitting and will be neglected till a later stage so we consider

$$\mathcal{H} = \sum_{i=1}^{n} \left[-\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} \right] + \sum_{i>j}^{n} \frac{e^2}{r_{ij}} . \qquad (2)$$

It is possible to solve the corresponding Schrödinger equation by making the one-electron approximation, in which the wave-function of the atom is made up of a linear combination of products of one-electron orbitals. In order to satisfy the requirement that the total electronic wave-function

be antisymmetric we must take combinations expressible as sums of Slater determinants. For example, if we have n electrons labelled 1, 2, ..., n, which can be in orbitals ψ_1, ψ_2, ..., ψ_n, containing both space and spin coordinates, the wave-function will be

$$\psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) \ldots \psi_1(n) \\ \psi_2(1) & \psi_2(2) \ldots \psi_2(n) \\ - - - - - - - - - - - - - \\ \psi_n(1) & \psi_n(2) \ldots \psi_n(n) \end{vmatrix} . \tag{3}$$

This is antisymmetric, for interchange of two electrons interchanges two columns of the determinant, changing the sign of ψ. Moreover if two orbitals are identical in both spin and space components the determinant vanishes, so the Pauli exclusion principle is satisfied.

Suitable one-electron orbitals for use as basis functions, the ψ_1 of Eq. (3), are obtained as eigenfunctions of the central field problem. Each electron is regarded as moving in a potential produced by the nucleus and a spherically averaged potential arising from all the other electrons. The corresponding Schrödinger equation is separable into one-electron equations, which, neglecting spin-orbit interaction, have the form

$$\left[-\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right] \psi_i = E_i \psi_i . \tag{4}$$

In general the potential U will be different for each orbital. Equation (4) is separable into radial and angular parts and has solutions

$$\psi_i = R_{n\ell}(r_i) \, Y_\ell^{m_\ell}(\theta_i, \varphi_i) , \tag{5}$$

where R is a radial function depending on $U(r_i)$, Y is a normalized spherical harmonic, and θ_i, φ_i are the angular co-ordinates. The solutions are characterized by quantum numbers n, ℓ and m_ℓ, all of which are integers. Of these, ℓ is the quantum number of orbital angular momentum, with maximum value n-1, and m_ℓ is the quantum number of a particular component (conventionally the z-component) of this orbital angular momentum. The

allowed values of m_ℓ are $|\ell|$, $|\ell|-1$, $\ldots$, $-|\ell|$. The remaining quantum number, n, occurs in the radial part of the function, which has $n-\ell-1$ nodes. It is usually called the principal quantum number, since the eigenenergy $E(n,\ell)$ is mainly determined by n, and to a lesser extent by ℓ.

It is customary to denote the value of ℓ by a letter according to the following scheme:

Value of ℓ -	0	1	2	3	4	5	6
Designation -	s	p	d	f	g	h	i
Degeneracy -	2	6	10	14	18	22	26 .

The degeneracy arises because the eigenenergies of Eq. (4) do not involve m_ℓ, which has $2\ell+1$ possible values. In addition, the electron has a spin whose z-component has a quantum number m_s, which can take either of the two values $\pm\frac{1}{2}$. Hence the degeneracy is $2(2\ell+1)$. This degeneracy is the total number of different combinations of m_ℓ, m_s for given values of n and ℓ, and so by the Pauli principle is the maximum number of electrons in the $n\ell$ shell. For example, if n=3 then ℓ can be 0, 1, or 2, so there will be a 3s shell which can accommodate two electrons, a 3p shell which can accommodate six, and a 3d shell which can accommodate ten. A closed shell is one which contains the maximum permitted number of electrons.

The central-field orbitals are therefore the familiar $n\ell$ orbitals of chemistry, each with quantum numbers (n,ℓ,m_ℓ,m_s) and with energies $E(n,\ell)$ which are the same for all electrons in a given shell. In a many-electron atom the orbitals will be filled, starting with the lowest in energy and going on up in energy, until all the electrons are accounted for. There is some regularity in the way this is done as the number of electrons increases, since the energies of the lowest shells increase with n, and for a given n increase with ℓ. The Periodic Table is a reflection of this regularity. Hydrogen is 1s, helium is $1s^2$, lithium $1s^2 2s$, beryllium $1s^2 2s^2$, boron $1s^2 2s^2 2p$ and so on, where a superscript indicates the number of electrons in the shell. When the d and higher shells are reached the energies no longer increase in this particular order. Argon has a configuration $1s^2 2s^2 2p^6 3s^2 3p^6$. Potassium, the next in the series, has a 4s electron, instead of 3d. Calcium has $4s^2$, and it is only with scandium, $3d4s^2$, that the 3d shell begins to be occupied. (We omit

listing all the closed shells in the notation.) In this way we get the first transition metal series, scandium to copper, in which the 3d shell is gradually filled while one or two electrons remain in the 4s shell. Similarly the second transition series, yttrium to silver, corresponds to filling the 4d shell; the rare earths, cerium to lutecium, to filling 4f; the third transition series, lanthanum to gold, to filling 5d; and the actinides, thorium to lawrencium, to filling 5f, and in each case there are generally one or more electrons in shells with higher principal quantum number.

So far so good, but the $(n\ell m_\ell m_s)$ orbitals are solutions of the central-field Eq. (4), not of the Hamiltonian of Eq. (2). We treat the difference in the Hamiltonians

$$\sum_{i=1}^{n} \left[-\frac{Ze^2}{r_i} - U(r_i) \right] + \sum_{i>j}^{n} \frac{e^2}{r_{ij}} \tag{6}$$

as a perturbation, taking Slater determinants of central-field orbitals as basic functions. Fortunately most of the electrons are usually in closed shells, and those which are not often have the same $n\ell$ values, or perhaps have two different $n\ell$ values. For example Co^{2+} has seven electrons in a 3d shell in its ground state, all the others being in closed shells, but there are excited states which may be of interest with configuration $3d^6 4p$. Now the interaction (6) will remove some of the degeneracy of the partially filled shells, but the closed shells simply contribute an energy shift which is the same for all levels of a given $n\ell$ partially-filled shell. (However, the shift will be different for different values of $n\ell$.) So if we are just interested in the energies of excited states relative to some ground state this uniform shift is absorbed by our choice of energy zero, and the closed-shell contribution can be ignored. Similar considerations apply to the spherically symmetrical part of (6). It is therefore only necessary to consider the perturbation e^2/r_{ij} summed over electrons in partially filled shells, and the problem is thereby considerably simplified.

In order to classify the resultant energy levels we consider the total angular momentum of the many-electron atom. There are four angular

momentum operators which commute with the Hamiltonian (2), namely the square of the total orbital angular momentum $\underset{\sim}{L}^2$, with quantum number L, the z-component of orbital angular momentum $\underset{\sim}{L}_z$, with quantum number M_L, and the corresponding spin operators $\underset{\sim}{S}^2$ and $\underset{\sim}{S}_z$ with quantum numbers S and M_S. A state characterized by the four numbers SLM_SM_L will satisfy the equations

$$\left.\begin{array}{l} \underset{\sim}{L}^2 \, |SLM_SM_L> \, = \, \hbar^2 \, L(L+1) \, |SLM_SM_L> \\[2em] \underset{\sim}{L}_z \, |SLM_SM_L> \, = \, \hbar M_L |SLM_SM_L> \\[2em] \underset{\sim}{S}^2 \, |SLM_SM_L> \, = \, \hbar^2 S(S+1) \, |SLM_SM_L> \\[2em] \underset{\sim}{S}_z \, |SLM_SM_L> \, = \, \hbar M_S \, |SLM_SM_L> \end{array}\right\} \tag{7}$$

where for later convenience we have used Dirac's notation. The angular momentum is the resultant of that of the one-electron orbitals, so for instance

$$M_L = \sum_{i=1}^{n} m_{\ell i} \; . \tag{8}$$

Here, as elsewhere, we use capital letters for many-electron quantities and small letters for one-electron quantities. Closed shells give zero contribution to sums of the type (8), so again only electrons outside closed shells have to be taken into account.

By adding the orbital and spin angular momenta we obtain the total angular momentum $\underset{\sim}{J}$,

$$\underset{\sim}{J} = \underset{\sim}{L} + \underset{\sim}{S} \; . \tag{9}$$

This method of forming $\underset{\sim}{L}$ and $\underset{\sim}{S}$ separately by equations of the type (8), and subsequently finding their resultant, is called Russell-Saunders coupling. The eigenvalue equations for $\underset{\sim}{J}^2$ and $\underset{\sim}{J}_z$ are exactly the same as those for $\underset{\sim}{L}^2$ and $\underset{\sim}{L}_z$, the quantum numbers being denoted by J and M respectively. It is therefore possible to label the states of the atom by

SLM_SM_L or by SLJM. Clearly the two alternatives are not independent. Note that L is necessarily integral, but S and J may be half-integral.

The electrostatic interaction (6) splits states with different S, L values but is independent of M_S, M_L, so now we have a set of energy levels, each labelled by SL. The totality of states corresponding to one of these energy levels is called a term, and is denoted by the symbol ^{2S+1}L. Because the electrostatic interaction does not involve M_S or M_L each SL term will be $(2S+1)(2L+1)$-fold degenerate. Hund's rule states that the term of lowest energy will have the highest possible value of S, and then, within this restriction, the highest possible value of L. As an example, the terms of d^3 allowed by the Pauli principle are ^4F, ^4P, ^2H, ^2G, ^2F, ^2D twice, and ^2P. The terms with highest S are ^4F, ^4P, and of these ^4F has the higher L. The ground state will therefore be ^4F, with S = 3/2, L = 3 and a degeneracy 28, while the remaining terms will be excited states lying 10^4 - 10^5 cm^{-1} above the ground state.

To obtain the energies of the terms it is necessary to find matrix elements of e^2/r_{ij} between the states $|SLM_SM_L>$, these states being treated as sums of Slater determinants. It is a feature of the theory that, within the approximation of using central-field orbitals, angular dependencies can be treated exactly, whereas radial functions do not appear in simple form. Equation (5) illustrates the point: the angular function is a spherical harmonic, while the radial function depends on a potential which does not have a general form. As a result it is necessary to introduce parameters which represent radial integrals. These are the Slater-Condon parameters F^k, G^k (in which k is a superscript, not a power). Certain linear combinations of the F^k, G^k are more convenient for some purposes, and Slater-Condon parameters F_k, G_k, Racah parameters A,B,C for d^n configurations and Racah parameters E^0, E^1, E^2, E^3 for f^n configurations will be found in the literature. For a configuration of equivalent $n\ell$ electrons there are $\ell+1$ independent parameters, e.g. for d^n, ℓ is 2 and three parameters are required, while for f^n, ℓ is 3 and four are needed. As an example we take the d^2 configuration, which is split by electrostatic interaction into terms with the following designations and energies:

$$
\begin{array}{lll}
{}^1S & A + 14B + 7C \\[6pt]
{}^1G & A + 4B + 2C \\[6pt]
{}^1D & A - 3B + 2C & \qquad\qquad (10) \\[6pt]
{}^3P & A + 7B \\[6pt]
{}^3F & A - 8B
\end{array}
$$

Since A, B and C are positive, ${}^3F$ is the lowest term, in accordance with Hund's rule. Any transition between two terms of the configuration will have an energy which is simply the difference between the two term energies, and therefore will not contain A. In principle B and C can be found by numerical integration of Schrödinger's equation, but in practice one regards them as empirical parameters, obtained by comparing measured transition energies with expressions of the above sort. It is found that the ratio C/B usually lies between four and five, and if one has insufficient data to determine both B and C separately it is often sufficient to take their ratio to be 4.5.

In a semiconductor, the properties of a nearly filled valence band are more conveniently discussed in terms of a few holes than in terms of the many electrons present. It can be shown that a similar concept is valid for free atoms, and the properties of a nearly closed shell can be described as if it contained holes. For instance a closed d-shell contains ten electrons, so d^8 behaves as if it contained two holes. The terms and energies will then be the same as those for d^2 given in (10) above, apart from an additive constant. There exists, therefore, a certain symmetry in that the spectrum of d^9 is similar to that of d^1, the spectrum of d^8 is similar to that of d^2 and so on.

We come now to spin-orbit coupling, which is a relativistic effect, but which can be pictured roughly as the interaction between the magnetic moment of an electron and the magnetic field created by its orbital movement. Its magnitude increases rapidly with the nuclear charge, so for light atoms spin-orbit effects may be negligible, while for heavy atoms they may be as great as, or greater than, electrostatic effects.

Equations (7) and the corresponding ones for $\underset{\sim}{J}^2$, $\underset{\sim}{J}_z$ showed that it was possible to classify states by the quantum numbers SLM_SM_L or $SLJM$. The spin-orbit term can mix states of different L or S, and now only J and M are good quantum numbers. If spin-orbit effects are fairly small, as in the $3d^n$ series (where the energies are of the order of 10^2-10^3 cm^{-1}, compared to 10^4-10^5 cm^{-1} for electrostatic effects), then L,S will still be nearly good quantum numbers. An LS term will now be split into a number of levels, each of different J value. Such a level is labelled $^{2S+1}L_J$, and the collection of levels derived from a single term is called a multiplet. The energies are given by the formula

$$E(SLJM) = \frac{\lambda}{2} \left[J(J+1) - S(S+1) \right] , \qquad (11)$$

where λ is a constant depending on S,L and a radial integral over $\xi(r)$, which is the function appearing in Eq. (1). The difference in energy between level J and level J-1 is just λJ. This simple formula is known as the Landé interval rule. For a shell less than half filled, λ is positive so the level with smallest J lies lowest, while the reverse is true for a shell more than half filled. As an example, the lowest term of d^2 is ^3F, which can have J values ranging from L+S to L-S. The levels and energies will therefore be

$$\left. \begin{array}{ll} ^3F_4 & \frac{5}{2}\lambda \\[2ex] ^3F_3 & -\frac{3}{2}\lambda \\[2ex] ^3F_2 & -\frac{9}{2}\lambda \end{array} \right\} \qquad (12)$$

The interval $^3F_4 - {}^3F_3$ is 4λ and the interval $^3F_3 - {}^3F_2$ is 3λ, in accordance with the Landé rule, and $^3F_2$ is the lowest level. For d^8, ^3F is still the lowest term and the scheme (12) still holds, but now λ is negative so $^3F_4$ is the lowest level.

When there are several LS terms close in energy, spin-orbit splittings may be comparable to the term separations, so strong mixing of the terms occurs. The LS labels are then poor descriptions of the states, although

they are customarily retained for convenience. Since spin-orbit coupling increases with nuclear charge, the levels of heavy elements may be far from pure LS states. Figure 8 shows the lower levels of $Co^{2+}(3d^7)$ and of $Er^{3+}(4f^{11})$, illustrating the fact that for $3d^n$ some lower terms remain clearly separated, while for $4f^n$ the spacing within a multiplet can be as big as the spacings between multiplets.
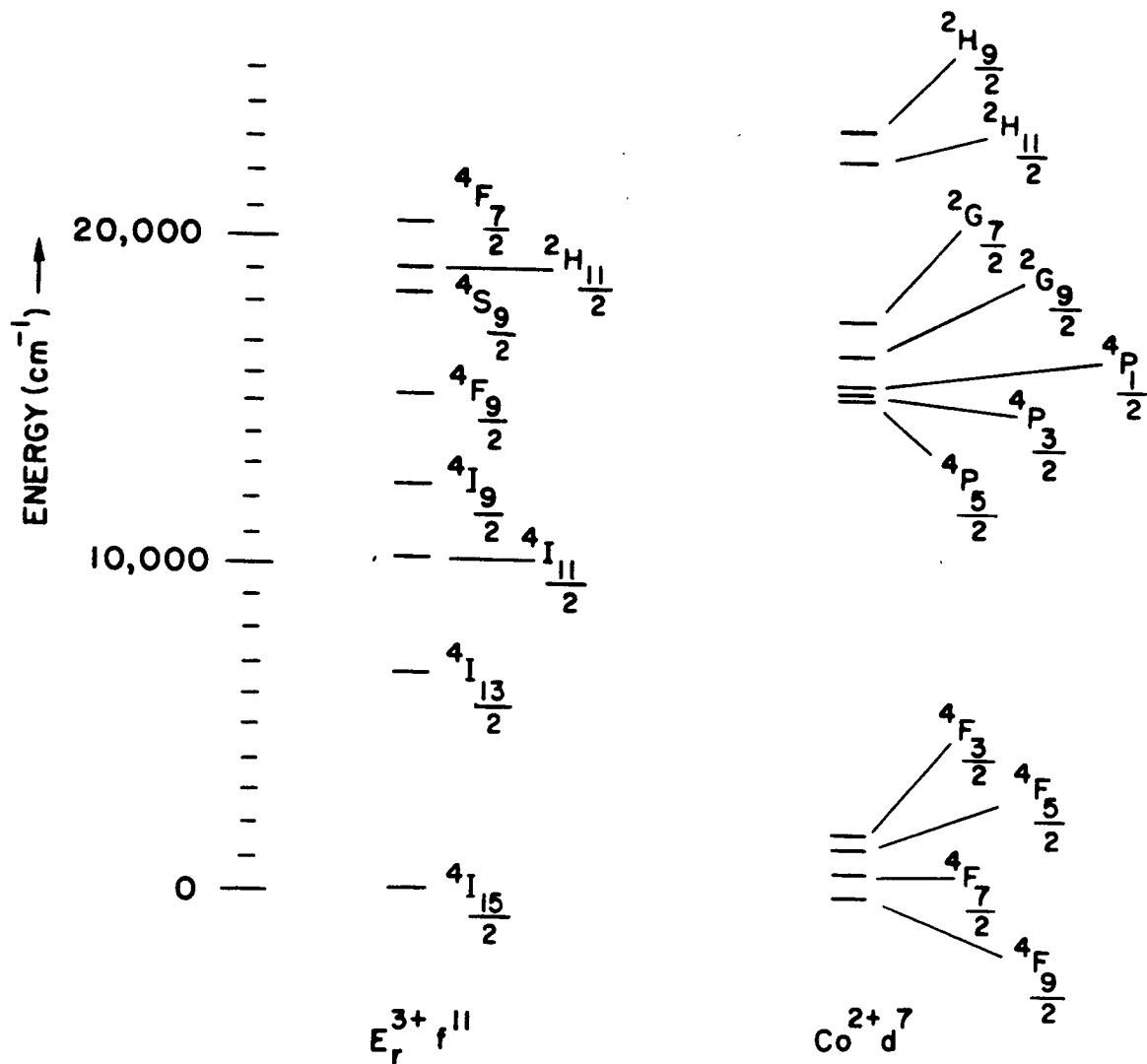
FIG. 8. THE LOWER LEVELS OF Co^{2+} AND Er^{3+}, SHOWING WELL-SEPARATED TERMS FOR 3d BUT NOT FOR 4f.

C.   The Crystal Field

So far we have discussed the properties of a free atom, and have considered the interaction of the electrons with a single nucleus and with each other. When the atom is incorporated as an impurity in a crystal there are a very large number of nuclei and of electrons, and the problem of finding the energy levels a priori is formidable. Fortunately, it turns out that some simple approximations, in which the crystalline environment is regarded as a perturbation on the free atom, often give a surprisingly good description for many systems of interest. Inner closed shells will be little affected by the environment except that their total energy may change somewhat. Outer orbitals used in bonding will have many of the properties of closed shells when combined with the crystal bonding orbitals: in particular, they will usually have zero total spin and total angular momentum, but they will not have spherical symmetry. Finally, there may be partially filled shells to be considered, and the discussion of this section will be centered on them. Just as in the case of the free atom, it is not possible to calculate the total energy with any great accuracy, and certainly not to within the 0.1 eV or so which we need in semiconductors, so again we have to absorb a large term by choosing a suitable zero of energy and content ourselves with calculating the small changes within the partially filled shells.

Some features of the treatment can be illustrated by a simple model. Suppose we have an impurity cation surrounded by a regular octahedron of anions as nearest neighbors; for example, an impurity replacing sodium in sodium chloride. Its site has octahedral symmetry, O_h in Schoenflies notation or m3m in International notation, and its properties must be invariant under all the symmetry operations of the site. If the impurity contains a single s-electron of given principal quantum number, then there will be only one spatial orbital in the free atom and this will have spherical symmetry. In the crystal, any symmetry operation turns the orbital into itself. If instead the impurity contains a single p-electron, then $\ell = 1$, so ℓ_z can have the values 1, 0, -1, i.e., there is three-fold spatial degeneracy in the free atom. It is possible to choose the three orbitals in such a way that they are aligned along the x, y and z axes as in Fig. 9. In the crystal we take these axes to be the axes of the

octahedron. Any symmetry operation will now turn any of these orbitals
into a linear combination of the set. For example, rotation about the
z-axis by $\pi/4$ turns p_x into $-p_y$, p_y
into p_x and p_x into p_z. Now suppose
the octahedron is distorted by com-
pression along the z-direction, so
the site symmetry is now D_{4h}
(Schoenflies) or 4/mmm (International).
The s-orbital still has the full
symmetry of the site and is still
singly degenerate spatially. On the
other hand, p_z is no longer equiva-
lent to p_x and p_y and we expect it
to have a different energy. The
three-fold degenerate p-level has
now split into a singly degenerate
level p_z and a doubly degenerate
level p_x, p_y. Correspondingly, we
find that under any symmetry opera-

FIG. 9. A SET OF p-ORBITALS,
p_x, p_y, p_z.

tion of the new site p_z turns into itself (apart from a possible change
of sign), while p_x and p_y turn into linear combinations of themselves.

From this example, we see that the number of levels and their de-
generacies are related to the symmetry properties of the site, while the
actual magnitude of the energy splittings must be found from other con-
siderations. Both aspects of the problem are rendered tractable if we
assume that the orbitals in the crystal can still be taken as combinations
of central field orbitals, and that the effect of the crystal can be
described by an electrostatic potential term V_{cf} in the Hamiltonian, the
subscript standing for crystal field.

The symmetry operators of the impurity site form a group in the
mathematical sense of the word. Any set of functions which turn into
linear combinations of themselves under any symmetry operation of the site
are a basis for a representation of the group. In the examples above, the
s-orbital is a basis for one representation of the octahedral group, and
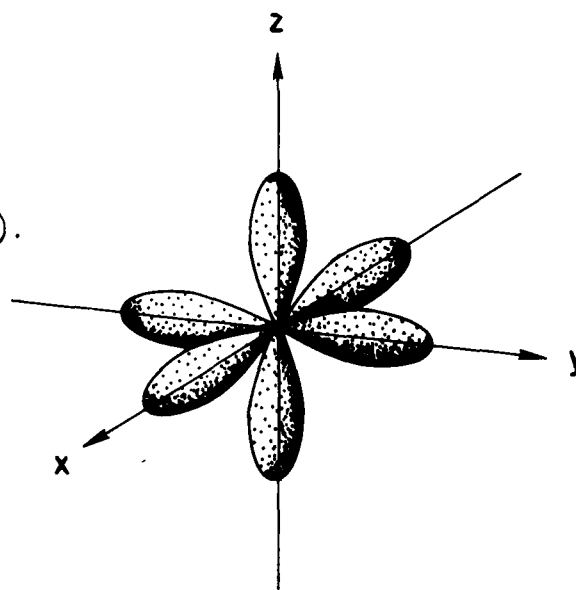the set of three p-orbitals are the basis for another. If the set of

functions can be decomposed into subsets such that the members of each subset turn into linear combinations of themselves only, then the representation is reducible. An irreducible representation is one which cannot be decomposed in this way. In the examples above, the three p-orbitals belong to a representation of the tetragonal group D_{4h} (4/mmm). This representation is reducible because there is a subset p_z and a subset p_x, p_y, and no symmetry operation of the site will transform a member of one subset into a member of the other set. Any set of wave-functions which have an intrinsic degeneracy, such as the three p-orbitals in octahedral symmetry, will belong to the same irreducible representation. The irreducible representations can therefore be used to label the set and their corresponding energy levels.

Because semiconductors with diamond or zinc-blende structure are so important, some detailed results will be given for them. A substitutional impurity is surrounded by a tetrahedon of nearest neighbors and has tetrahedral symmetry, T_d (Schoenflies), $\bar{4}$ 3m (International). In the absence of spin, there are five irreducible representations which, in Mulliken's notation are A_1, A_2, E, T_1, T_2. (Bethe's notation uses the symbols $\Gamma_1 - \Gamma_5$. Mulliken's notation is more informative - the degeneracy of A or B is one, that of E is two and that of T is three.) In the presence of spin there are extra symmetry elements giving the so-called "double group," with extra representations which are variously labelled $E_{1/2}$, $E_{5/2}$, G or E', E'', U, or Γ_6, Γ_7, Γ_8. They have degeneracies two, two and four respectively.

Orbitals with $\ell = 2$, i.e., those having the angular properties of d-orbitals, belong to a reducible representation. In the absence of spin-orbit effects, decomposition of the representation yields the irreducible representations E and T_2. Physically, this means that a single d-electron in a tetrahedral environment can have two possible energy levels, one being two-fold and the other three-fold degenerate. The energy difference between these two levels, i.e. the crystal field splitting, is denoted Δ (or sometimes as 10 Dq). The absorption spectrum of a d^1 configuration, therefore, consists of a single peak at energy Δ. Because of the symmetry between holes and electrons, the absorption spectrum of a d^9 configuration is also a single peak. The value of Δ of course depends on the impurity,

its charge state and its environment. Spin-orbit interaction produces
further, smaller, splitting, which we will not consider in detail here.

To find the energy levels of a d^n configuration, one can approach
the problem from two extremes. In the weak-field limit, when the crystal
field is much smaller than the d-d electrostatic interactions, one can
start with the states $|SLM_S M_L >$ and consider the effect of the crystal as
a perturbation. Although L is no longer a good quantum number, it is
nearly so. In the strong-field limit, one forms a configuration $e^m t_2^{n-m}$
from the individual crystal-field orbitals e and t_2, and then considers
the electrostatic interaction between them as a perturbation. (In the
rare earths, spin-orbit coupling is strong, while the 4f orbitals are
shielded and are not greatly influenced by the crystal. One then begins
with states $|SLJM >$ which are diagonal in the electrostatic and spin-orbit
terms of the Hamiltonian, and takes the crystal field as a perturbation.)
The resultant energies are expressed in terms of the Racah parameters
A, B, C and the crystal-field parameter Δ. If Δ and spin-orbit coupling
are small, then it is a useful approximation to use the quantum numbers
S and L, but the only exact quantum labelling is by the irreducible repre-
sentations.

A useful theorem is that the matrix element of an operator belonging
to the irreducible representation Γ_o, between states belonging to Γ_i, Γ_j,
i.e. $< \Gamma_i |\Gamma_o|\Gamma_j >$, vanishes unless the product $\Gamma_i \times \Gamma_o \times \Gamma_j$ contains the
totally symmetric representation A_1. Using this, one can deduce the
selection rules for optical absorption. In particular, allowed electric
dipole transitions, for which Γ_o is T_2, are given in Table 1.

TABLE 1. ALLOWED ELECTRIC DIPOLE
TRANSITIONS IN $T_d (\bar{4}\ 3m)$ SYMMETRY

$$A_1 \rightarrow T_2$$

$$A_2 \rightarrow T_1$$

$$E \rightarrow T_1 + T_2$$

$$T_1 \rightarrow A_2 + E + T_1 + T_2$$

$$T_2 \rightarrow A_1 + E + T_1 + T_2$$

In reality, of course, the impurity orbitals are not central-field ones, since the site does not have spherical symmetry. Also, it is a crude approximation to replace the crystal by an electrostatic potential. A more realistic model is that of the molecular orbital approach, in which one takes as a basis a set of orbitals which are not localized at any particular atom, but which extend over all the atoms present. To make the method tractable, it is necessary to limit the number of atoms considered to those in the immediate vicinity of the impurity. In semi-conductors this is equivalent to underestimating the conduction and valence band widths, often by an order of magnitude. In addition, it is necessary to construct the molecular orbitals by taking a linear combination of atomic orbitals or of some other simple functions. As a result, the molecular orbital approach is not yet capable of predicting the behavior of impur-ities in semiconductors, although it is sometimes useful in correlating observed results.

It is possible to make a general formulation of the crystal-field problem, without requiring central-field orbitals of a point-ion potential. Symmetry considerations limit the number of parameters needed. However, even if one restricts the problem to $e^m t_2^{n-m}$ configuration in $T_d(\bar{4}\,3m)$ symmetry, one needs nine independent parameters to specify the energies, which is always more than the experimental data can supply.

VI. APPLICATION OF CRYSTAL FIELD THEORY TO SEMICONDUCTOR PROBLEMS

A. Introduction

In this chapter the results of the theory outlined earlier will be applied to some problems concerning impurities in semiconductors, particularly $3d^n$ impurities in zinc-blende or wurtzite structures. Although electron spin resonance is interpreted within the framework of the same theory and has provided a great deal of information on the properties of impurities it will not be treated in detail here, since excellent review articles on the subject exist[6]. We shall confine our attention to optical and electrical properties.

We have seen that it is possible to obtain expressions for the energy differences within a d^n configuration, in the absence of spin-orbit coupling, in terms of the Racah parameters B and C, and a crystal field parameter $\triangle$. In order to do this one starts with central-field orbitals, which are then perturbed by the crystal field. The resulting energy expressions will, in general, contain a large number of parameters. By assuming that the central-field orbitals have the angular dependence of d-orbitals and that the radial part of the function is the same for all orbitals involved, it is possible to reduce the number of parameters to three, namely B, C, and $\triangle$. The assumptions are unjustifiable for strongly covalent materials. However, it is found that the expressions for energy differences give a good description of experimental results if B, C and $\triangle$ are taken as empirical parameters. The situation therefore is that application of crystal field theory to the materials considered here is logically untenable but is experimentally useful. More refined theories, such as molecular-orbital theory, are logically more satisfactory but have not yet reached the stage at which they can do more than roughly approximate the experimental results. We shall therefore use the simple crystal field theory in a semi-empirical manner. Of course the experimental results shed some light on the theory, and this will be briefly considered.

B. Electron Configurations

Transitions within a d-shell give rise to optical absorption. The energy levels depend on the number of d-electrons and the symmetry of the

impurity site. Optical absorption spectra can therefore be used to determine the electron configuration at an impurity.

Figure 10 shows the energy levels of d^n configurations in tetrahedral co-ordination as a function of crystal field, in the absence of spin-orbit splitting. Only levels with the same spin as the ground state are shown. Transitions between them are spin-allowed although subject to the symmetry
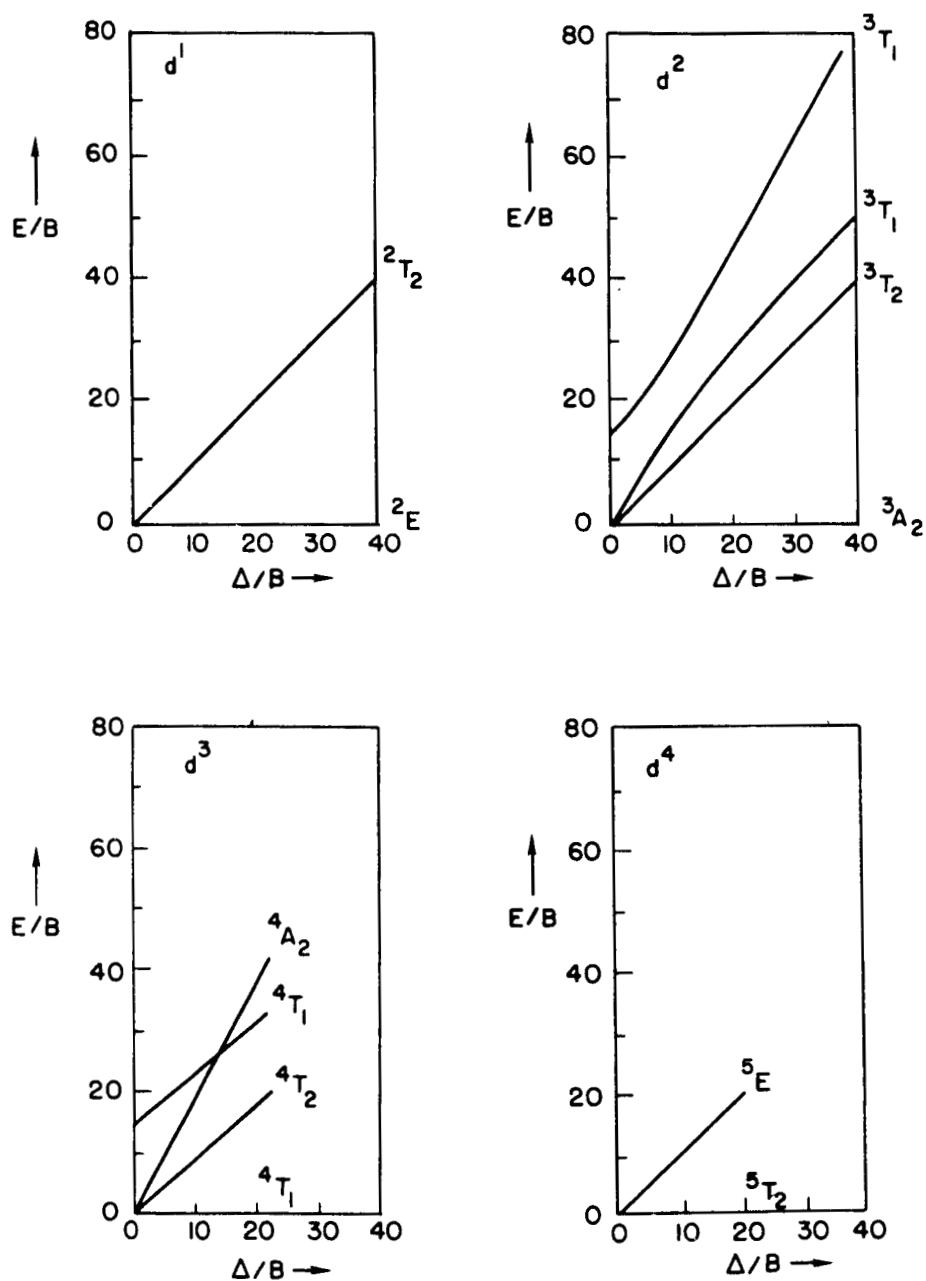
FIG. 10. CRYSTAL FIELD LEVELS OF MAXIMUM SPIN FOR d^n CONFIGURATIONS IN TETRAHEDRAL SITES. (Manganese has only one sextet state, so quartet levels are also shown.)
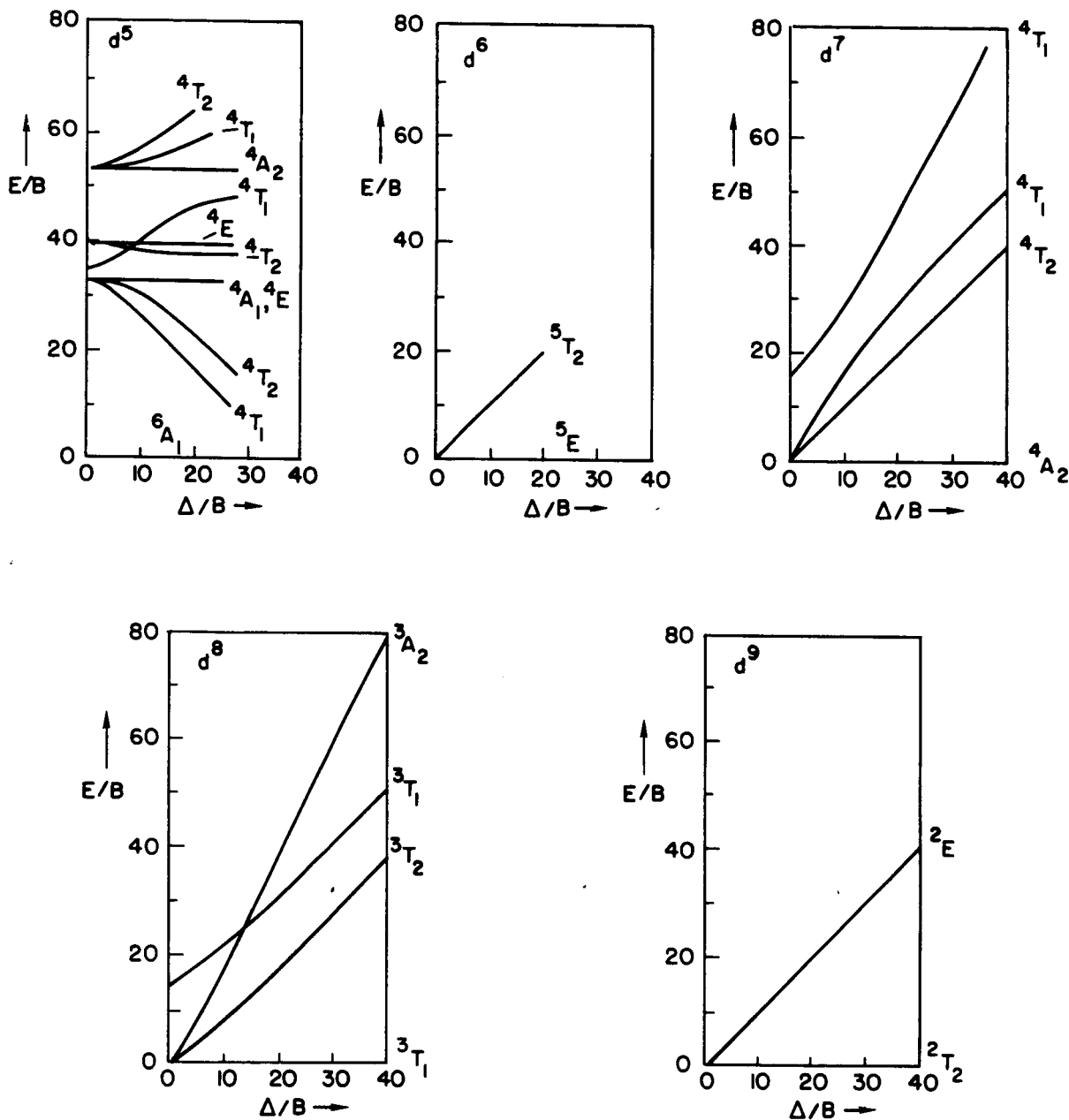
FIG. 10.   CONTINUED.

selection rules of Table 1, and will therefore contribute much more strongly to optical absorption than transitions to other levels of lower spin.   The form of the matrix elements is such that it is convenient to plot energy and crystal field in units of B.   In the case of d^5 the ground state is the only one with spin 5/2, so levels with spin 3/2 are also shown.

If an observed absorption spectrum can be fitted to one of these energy level schemes, it may be taken as evidence that the impurity has the corresponding electron configuration. As an example the absorption spectra of zinc selenide doped with various $3d^n$ impurities are shown in Fig. 11, together with assignments of the transitions involved[7].
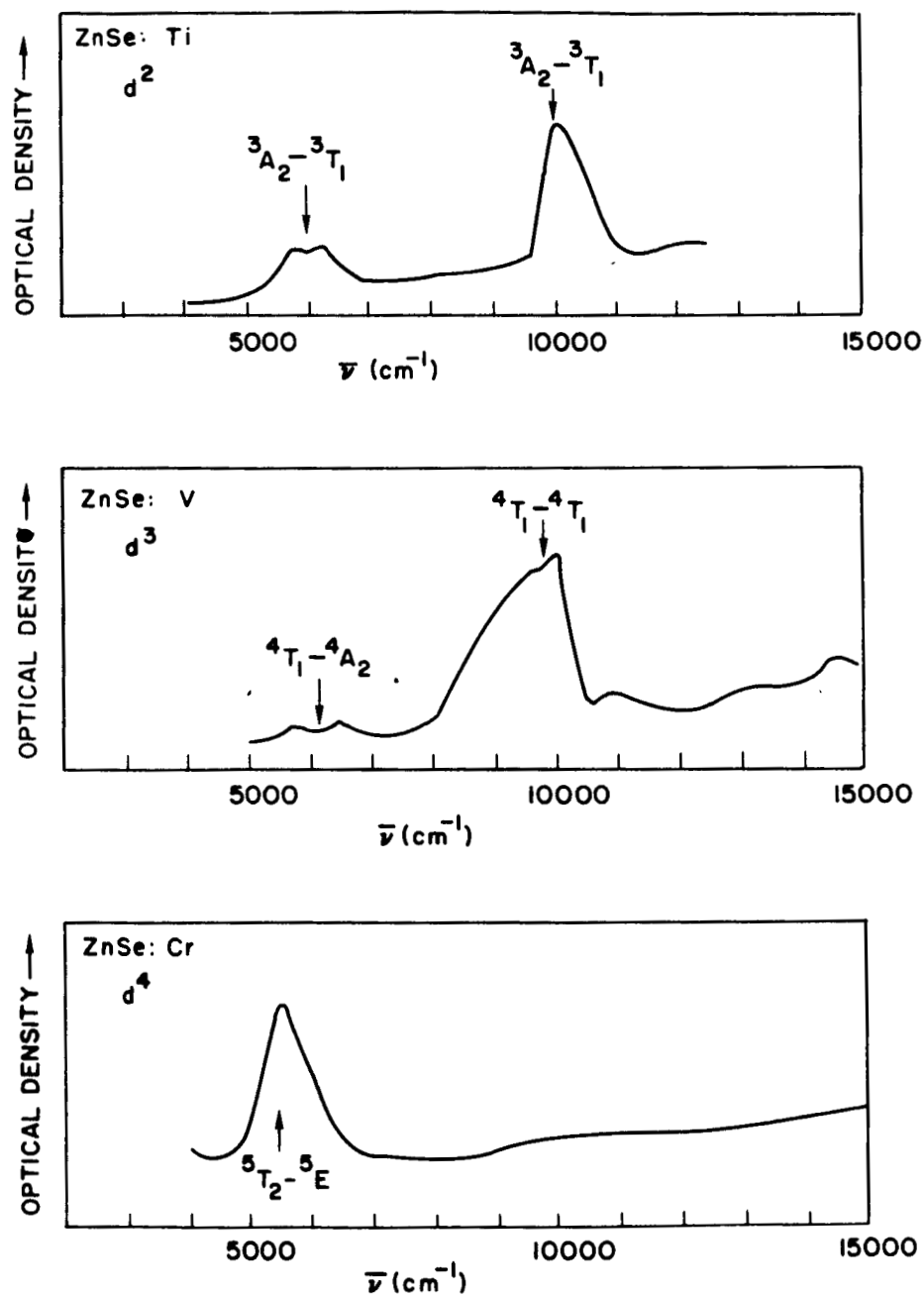
FIG. 11. ABSORPTION SPECTRA OF $3d^n$ IMPURITIES IN ZnSe.
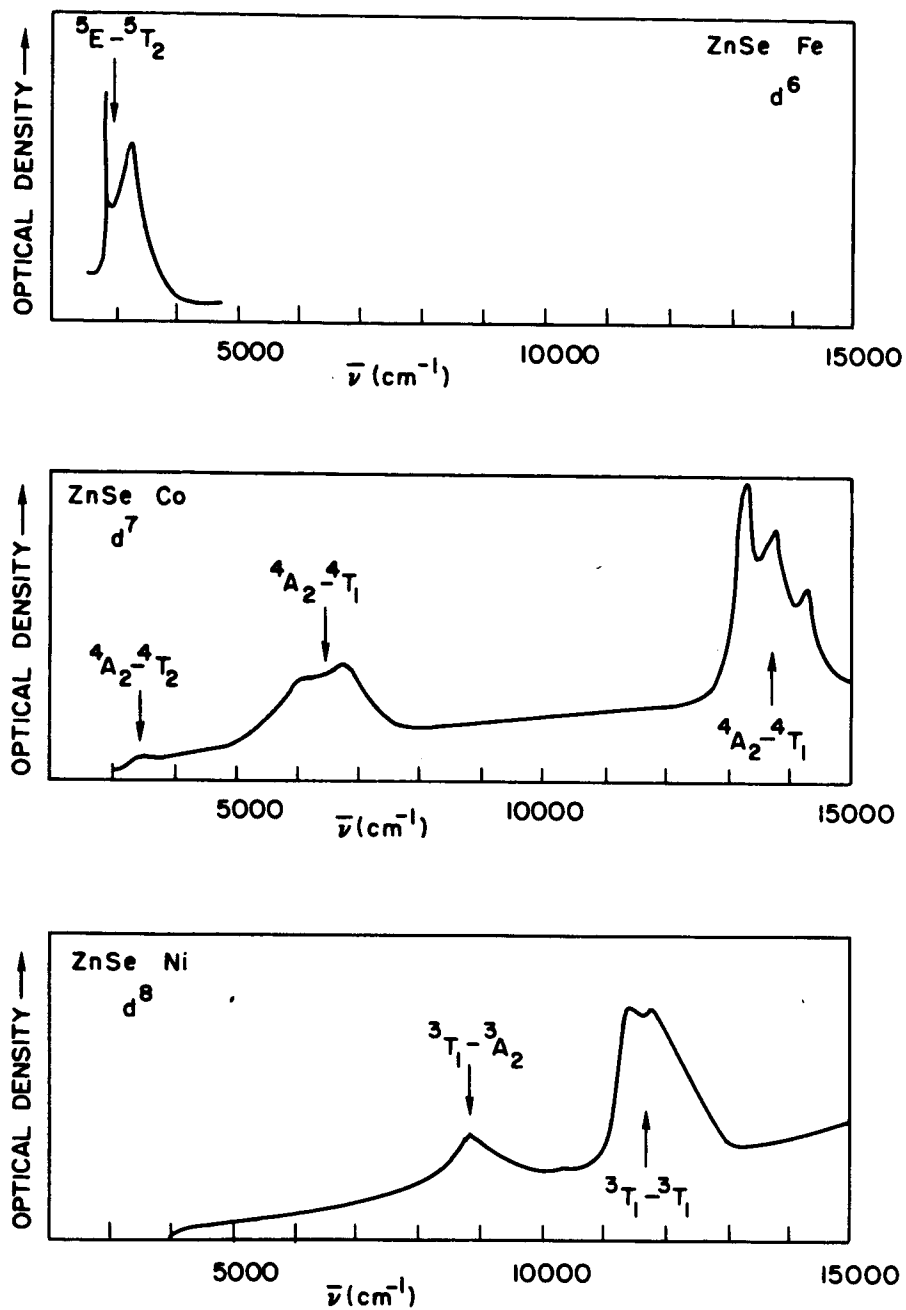
FIG. 11. CONTINUED.

The finer details of the spectra arise from spin-orbit splitting, phonon interactions, spin-forbidden transitions and Jahn-Teller distortions. An extensive theoretical treatment is required to take into account all these effects, but it can be seen from Fig. 11 that the first-order model gives an explanation of the main features.

It often occurs that no single piece of evidence is in itself sufficient to establish the electron configuration and symmetry site of an impurity. A number of different measurements may then be necessary. Loescher et al[8] have illustrated some of the methods of approach in their study of cobalt in gallium phosphide. By electrical measurements they find cobalt to be an acceptor impurity. When it has accepted an electron it has an optical absorption spectrum typical of d^7 in octahedral or tetrahedral coordination. The oscillator strength of a transition within the d-shell is typically $10^{-6} - 10^{-5}$ for octahedral and $10^{-4} - 10^{-2}$ for tetrahedral coordination. Loescher found the main absorption peak in GaP:Co had an oscillator strength of 8×10^{-4}, so the cobalt is at a tetrahedral site, but in the zinc-blende structure this could be either substitutional or interstitial. A free cobalt atom has seven d-electrons and two outer electrons, so after accepting an electron there will be ten electrons outside the inner closed shells. It is not possible to accommodate these electrons in orbitals such that there is a d^7 configuration with all other electrons in closed shells if the cobalt were interstitial. If the cobalt were substitutional, replacing gallium, then three electrons can go into bonding orbitals, leaving a d^7 configuration. By combining measurements of electrical properties, impurity concentration and optical absorption Loescher et al were therefore able to conclude that cobalt in gallium phosphide substitutes for gallium and, after accepting an electron, has a d^7 configuration with all the bonding orbitals filled.

C.   Values of the Parameters

The interpretation of an absorption spectrum is easier when one knows approximately the magnitudes of the parameters B, C and $\triangle$ which would be expected for a given system. These can often be found by extrapolation from known values for similar systems.

By now there have been several investigations of $3d^n$ impurities in the II-VI compounds. Some of the results obtained are given in Tables 2-5. When a particular impurity in a particular compound has been investigated by different workers then the discrepancies in the reported parameters give an idea of the accuracy involved. Some energy separations are insensitive to the parameter values. This is particularly true of the lower

TABLE 2. ZnO

	Impurity	Δ (cm^{-1})	B (cm^{-1})	C/B	Ref.
d^7	Co	3900	775	4.5	1
"	"	3900	700		2
d^8	Ni	4200	770	4.8	1
"	"	4050	795	4.36	3
d^9	Cu	5000			1
"	"	5690			4

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TABLE 3. ZnS

	Impurity	Δ (cm^{-1})	B (cm^{-1})	C/B	Ref.
d^5	Mn	5200	583	5.35	1
"	"	4400	762	3.58	2
d^6	Fe	3400			3
d^7	Co	3750	610	4.4	4
d^8	Ni	4750	560	4.5	4
d^9	Cu	6240			5
d^2	V	5500	456		6

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TABLE 4. ZnSe

	Impurity	$\Delta\ (cm^{-1})$	$B\ (cm^{-1})$	C/B	Ref.
d^2	Ti	3750	330		1
d^3	V	3350	460		1
d^4	Cr	5600			1
d^5	Mn	4050	741	3.7	2
d^6	Fe	3150			4
d^7	Co	3800	570		4
d^8	Ni	4350	510		1
d^2	V	5150	456		3

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3. J. W. Allen, Physica 29, 764 (1963).

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TABLE 5. CdS

	Impurity	$\Delta\ (cm^{-1})$	$B\ (cm^{-1})$	C/B	Ref.
d^4	Cr	5320			1
d^6	Fe	2800			5
d^7	Co	3300	610	4.4	2
"	"	3160	664	4.5	1
d^8	Ni	4000	570	4.7	2
"	"	4150	615	4.4	1
d^9	Cu	5560			3
d^2	V	4800	456		4

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levels of d^5. Langer and Ibuki[9] and Ford et al[10] give
widely different values of B and $\triangle$ for manganese in ZnS. Both sets of
values give about equally good fit to the first three absorption peaks
observed experimentally, and only by going to higher energy absorption
peaks can one see that the interpretation of Ford et al may be preferable.

We have extended the field of investigation to the III-V compounds
by studying the absorption spectra of chromium $\left(d^4\right)$, iron $\left(d^6\right)$, cobalt
$\left(d^7\right)$ and nickel $\left(d^8\right)$ in gallium phosphide. This material has a band gap
of 2.25 eV at room temperature and so is transparent throughout most of
the optical region in which crystal field spectra occur. Unfortunately
in some of the III-V compounds, such as GaAs, and in silicon and germanium,
most crystal-field spectra would be completely masked by band-to-band
absorption.

A large body of data has been accumulated concerning the absorption
spectra of transition-metal complexes. Jørgensen[11] and others
have pointed out the existence of empirical correlations of B and $\triangle$ with
quantities such as the electronegativity of the ligands. These corre-
lations cannot be extrapolated to the strongly covalent, tetrahedrally
coordinated materials with which we deal here, but instead we have observed
new ones.

The values of $\triangle$ for divalent $3d^n$ ions in II-VI compounds are plotted
in Fig. 12. It will be seen immediately that $\triangle$ for a given impurity
varies by only a small amount from compound to compound. The variation
of $\triangle$ with number of d-electrons shows a definite pattern, and is roughly
symmetrical about the middle of the series. (The discrepancy in the values
for manganese was discussed above.) Our preliminary values of $\triangle$ for im-
purities in gallium phosphide follow the same pattern but lie higher by
about 1000 cm^{-1}. In this case the impurities have accepted an electron
and therefore have a negative charge with respect to the lattice.
Vanadium occurs in ZnSe in either divalent $\left(d^3\right)$ or trivalent $\left(d^2\right)$ form,
depending on the position of the Fermi level. Vanadium $\left(d^2\right)$ has a positive
charge with respect to the lattice, and has a value of $\triangle$ which is 1800 cm^{-1}
greater than for neutral vanadium $\left(d^3\right)$. Although more data are needed, it
appears that $\triangle$ is greater for charged impurities than for neutral ones,
irrespective of the sign of the charge.
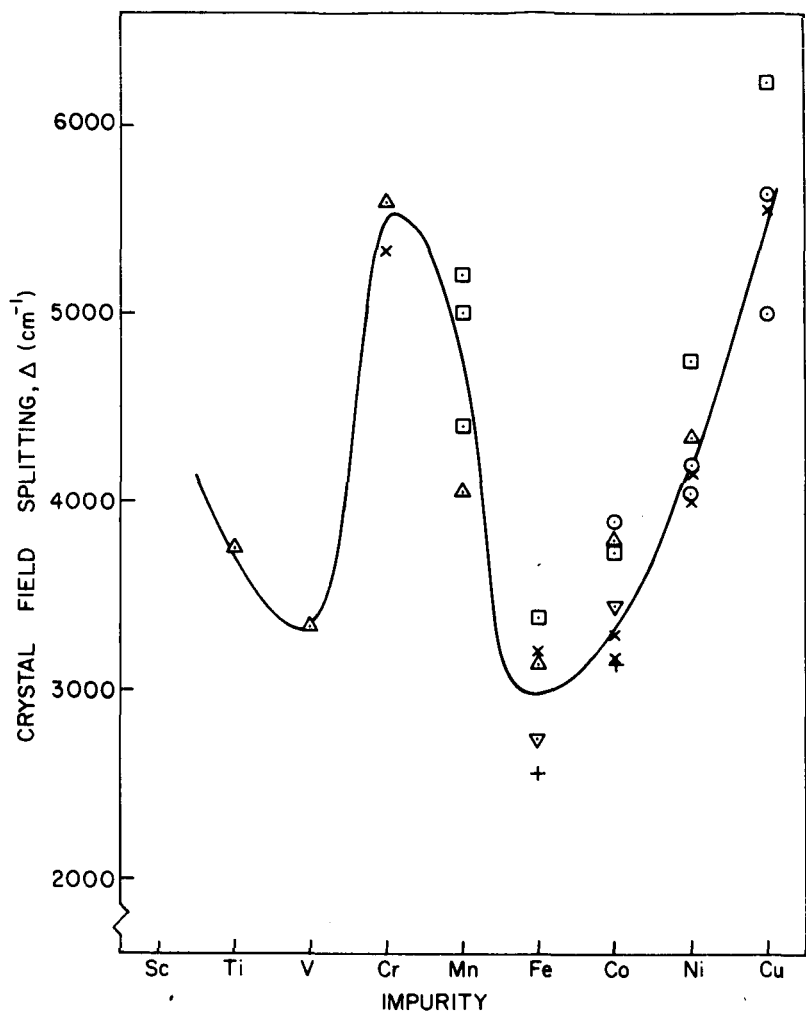
FIG. 12. VARIATION OF THE CRYSTAL FIELD SPLITTING
Δ THROUGH THE FIRST TRANSITION SERIES FOR
IMPURITIES IN II-VI SEMICONDUCTORS.

Key: ⊙ ZnO   ▼ ZnTe

      ◉ ZnS   ✕ CdS

      ▲ ZnSe   + CdTe

It is well known that in compounds the Racah parameter B is reduced
from its free ion value. We define a Racah parameter reduction factor β
as being the ratio of B for an impurity in a crystal to B for a free ion.
In complexes and fairly ionic compounds like halides β may be about 0.9,
but in the II-VI and III-V compounds β can be less than 0.5. Various
mechanisms have been proposed to explain the effect. Radial expansion

of the d-orbitals, covalent mixing of d-orbitals with bonding orbitals and screening of d-d electron interactions by bonding electrons no doubt all play a part. However, no quantitative theory of the effect exists as yet.

Weakliem[12] proposed an empirical correlation of β with anion polarizability of the host lattice. The refractive index n is a related but more readily accessible parameter, especially for III-V compounds. Figure 13 is a plot of β against n^{-2} for cobalt in a number of II-V
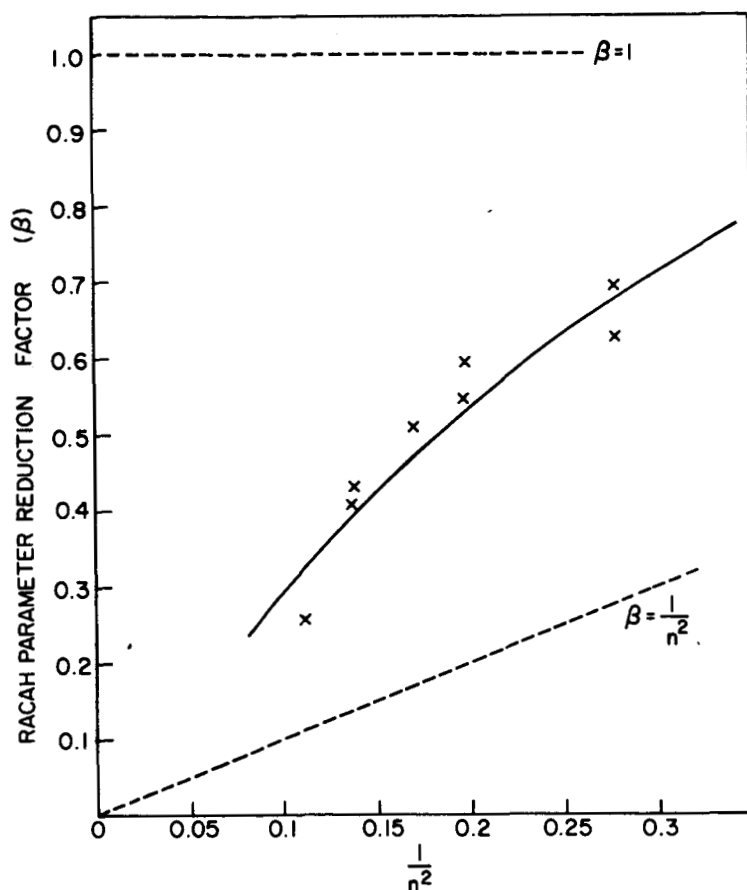
FIG. 13. VARIATION OF THE RACAH PARAMETER REDUCTION FACTOR β WITH n^{-2}, WHERE n IS THE INFRA-RED REFRACTIVE INDEX, FOR $Co(d^7)$.

compounds and in GaP. The experimental points lie on smooth curves. Also shown are the lines $\beta = 1$ and $\beta = n^{-2}$. Suppose that the Racah parameter reduction is attributable to screening by the valence electrons, and that the screening is describable by the introduction of a dielectric constant. A self-consistent relation would require that when there is strong screening

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the d-orbitals expand and, in the limit, expand so far that the appropriate dielectric constant is the bulk value, n^{-2}. Conversely, when the d-orbitals are tightly bound so that they are not much affected by the valence electrons then the appropriate dielectric constant is unity. So the curve relating β to n^{-2} lies between the lines $\beta = 1$ (which it approaches at one extreme) and $\beta = n^{-2}$ (which it approaches at the other extreme). Although this reasoning indicates that the observed variation is physically reasonable, it must not be taken too literally.

As yet there are insufficient data to draw any reliable conclusions concerning the way in which β varies with the number of d-electrons. Similarly it is not possible to say anything about how the Racah parameter C varies from compound to compound or impurity to impurity, except that the ratio C/B is usually between 4 and 5, as it is in the free ions.

Empirical correlations of the above type may indicate which are the important factors to be considered in a theoretical treatment of ions in covalent crystals. For instance, the fact that Δ is roughly constant for a given impurity, independent of the host crystal, suggests that the origin of the crystal field lies predominantly in the interaction of the d-orbitals with sp^3 bonding orbitals centered on the impurity itself. For our purposes, however, the correlations are of utility in allowing us to predict crystal field energy levels in systems not yet investigated, thereby simplifying the problem of interpretation.

D. Luminscence

Since the early work of Kröger[13] in 1939 it had been suspected that the luminescence of ZnS:Mn was due to transitions within the d-shell. This luminescence has characteristics which distinguish it from the band-to-impurity luminescence of say ZnS:Cu. The excitation spectrum consists of a number of rather narrow bands with energies less than the energy gap of the host lattice. The decay is exponential with a time constant which is little affected by factors such as the presence of other impurities. The efficiency remains relatively constant up to temperatures of 250°C,[14] while band-to-impurity luminescence is often strongly quenched at 100°C.

In 1955 Orgel[15] published crystal field energy level diagrams for $3d^n$ ions and attributed the luminescence of divalent manganese salts to

the $^4T_1 - {}^6A_1$ transition (see Fig. 10). The excitation bands correspond to absorption to higher crystal field levels. Since then, luminescence from d-shell transitions has been observed for $V(d^2)$, $Mn(d^5)$, $Co(d^6)$, and $Cu(d^9)$ in various II-VI compounds: a list is given in Table 6. (It is possible

TABLE 6. LUMINESCENCE OF $3d^n$ IMPURITIES IN
II-VI COMPOUNDS

System	$3d^n$	Assignment	References
ZnS:V	d^2	$^3T_2(F) - {}^3A_2(F)$	1,2,3
ZnSe:V	"	"	"
CdS:V	"	"	"
CdSe:V	"	"	"
ZnS:Mn	d^5	$^4T_1(G) - {}^6A_1(S)$	4,5
ZnSe:Mn	"	"	"
CdS:Mn	"	"	"
ZnS:Co	d^7	$^4T_1(F) - {}^4T_2(F)^*$	7,8,9
		$^4T_2(F) - {}^4A_2(F)^*$	
ZnS:Cu	d^9	$^2E(D) - {}^2T_2(D)$	10
CdS:Cu	"	"	"

*In dispute. See text.

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2. M. Avinor, G. Meijer, J. Phys. Chem. Solids 12, 211 (1960).

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9. G. F. J. Garlick, M. J. Dumbleton, Proc. Phys. Soc. 67B, 442 (1954).

10. I. Broser, H. Maier, H.-J. Schulz, Phys. Rev. 140A, 2135 (1965).

that the red emission of ZnS:Fe[16] is due to transitions within d^5.)
Usually it is a straightforward matter to identify the transition by comparing its energy with the calculated crystal field levels.

If the optical transition is forbidden then the observed radiation may be the result of strong phonon coupling, with a large Franck-Condon shift as a consequence. The $^4T_1 - {}^6A_1$ transition in $Mn(d^5)$ is spin forbidden. In ZnS:Mn the emission peak is at 17,000 cm^{-1} (5860 Å), while the corresponding absorption peak is at 18,700 cm^{-1} (5350 Å), a shift of 10 percent. Langer and Ibuki[9] demonstrated the identify of the emission and absorption by observing the zero-phonon line. When this cannot be done, there may be uncertainty in the assignment of the transition.

The problems that arise are illustrated by the case of ZnS:Co.[17] The excitation spectrum consists primarily of two bands corresponding to transitions from the $^4A_2$ ground state to the two $^4T_1$ levels of the d^7 configuration (Fig. 10). Emission is seen near 3μ. Two possible assignments are shown in Fig. 14. Gumlich and Schulz[18] argue for the first of these, in which the fine structure in emission is attributed to phonon side-bands, on the grounds that the energy of the emission peak is close to that of the $^4A_2 - {}^4T_2$ transition seen in absorption. Two objections may be raised against this assignment. Firstly, the emission spectrum is unchanged between 5°K and 76°K, which is inconsistent with the expected change of phonon population with temperature. Secondly, an $A_2 - T_2$ transition is forbidden by symmetry, so the oscillator strength is small. Using the Einstein relation between absorption and emission probabilities one can calculate a radiative decay time of about 10 msec: the measured value is two orders of magnitude smaller. A large Franck-Condon shift could explain the discrepancy,[19] but the agreement between the observed absorption and

FIG. 14. POSSIBLE ASSIGNMENTS OF THE LUMINESCENT TRANSITION IN ZnS:Co.

emission peaks then becomes a difficulty. The second assignment of Fig. 14 attributes the fine structure seen in emission to spin-orbit splitting of the $^4T_2$ level. This explains the observed constancy of the emission spectrum at low temperatures. At room temperature the higher components of $^4T_1$ will be populated, with a consequent change in the spectrum. Although this assignment removes the difficulties encountered by the other one, more data are needed to settle the matter unambiguously.

Unfortunately, for $3d^n$ impurities in II-VI or III-V compounds, we have no means at present of predicting which transitions will be predominantly radiative and which will be predominantly nonradiative. When there is a large energy gap between one level and the next, nonradiative transitions will be improbable because of the large number of phonons involved. The $^4T_1$ level of $Mn(d^5)$ in ZnS lies 18,000 cm^{-1} above the $^6A_1$ ground-state. A nonradiative transition would require the emission of about fifty phonons, an unlikely event, so the transition is radiative. When the separation is smaller no such rule applies. A striking example of the problem is the luminescence of $V(d^2)$ in say ZnS. There are six possible transitions within the triplet levels, but radiation has been observed from only one of these (Table 6), and this happens to be symmetry-forbidden for electric dipole radiation, while the others are allowed. The question is not only of scientific interest but also of technological importance. Iron, cobalt and nickel are "killers" of luminescence in such phosphors as ZnS:Ag, i.e. they can strongly decrease the efficiency of visible luminescence when they are present in amounts of the order of a few parts per million. It is therefore necessary to take stringent precautions to exclude them when making efficient phosphors, or to control their amounts when making use of them, as for example in the manufacture of short after-glow phosphors. In the absence of any detailed understanding of nonradiative processes, all such things have to be carried out on a purely empirical basis.

E. Observed Configurations

We recall that if the orbitals are divided into d-orbitals and host-crystal orbitals, then the following possibilities exist:

a)   All bonding orbitals full, plus a partially filled d-shell.

b) A hole in the valence orbitals, bound in a "hydrogen-like" state, plus a partially filled d-shell.

c) An electron in the conduction orbitals, bound in a "hydrogen-like" state, plus a partially filled d-shell.

The actual orbitals will be mixtures of d-orbitals and bonding or conduction band orbitals, with the above possibilities as the limiting cases when a mixing coefficient becomes zero.

Ludwig and Woodbury[20] proposed that substitutional $3d^n$ impurities in germanium and silicon retain filled bonding orbitals, and that the numerous charge states observed correspond to having different numbers of electrons in the d-shell. Interstitial impurities have no bonding and the outer 4s electrons collapse into the 3d shell. The evidence for these models comes from spin resonance data. Table 7 shows the observed charge states and the $3d^n$ configurations which they deduce from the resonance spectra. The information given is for isolated impurities: interstitial impurities in silicon have a strong tendency to form pairs with other impurities, which complicates the picture.

TABLE 7. CONFIGURATIONS OF ISOLATED $3d^n$ IMPURITIES IN SILICON AND GERMANIUM

Silicon, interstitial	V^{2+}	d^3
	Cr^+	d^5
	Cr^o	d^6
	Mn^{2+}	d^5
	Mn^+	d^6
	Mn^o	d^7
	Mn^-	d^8
	Fe^+	d^7
	Fe^o	d^8
	Ni^+	d^9
Silicon, substitutional	Cr^o	d^2
	Mn^+	d^2
	Mn^{2-}	d^5
Germanium, substitutional	Mn^{2-}	d^5

Table 8 lists $3d^n$ configurations which have been observed in the II-VI compounds and in GaAs and GaP. For most entries it has been confirmed that the impurity is substitutional and isolated. Again it appears that a model in which the bonding orbitals remain filled, while the d-shell occupancy can change, is often valid.

Manganese in GaAs is at the opposite extreme for it behaves like a shallow acceptor. Anderson[21] has shown, by studying the intensity of the phonon side-bands in the luminescence spectrum, that the hole orbit has a radius more appropriate to that of a hydrogen-like orbital, rather than that of a d-orbital. Similarly copper in InSb[22] gives rise to two shallow acceptory levels, probably helium-like. The problem of whether a normally divalent impurity in a III-V compound will produce a deep level or a hydrogen-like level will be discussed in Section F. For reasons which will emerge from that discussion, shallow donors will not be produced by substitutional $3d^n$ impurities in II-VI or III-V compounds, except for impurities close to the beginning of the series, such as scandium, in II-VI compounds. However, a deep level with a $3d^n$ configuration should always have an excited state with a $3d^{n-1}$ configuration together with an electron in a hydrogen-like orbit. These states have not yet been observed--if they could be seen by optical absorption, they would give a precise way of determining the energy of the deep level.

There is little information concerning systems which are intermediate between the extremes, i.e. systems in which a hole and a d-shell interact strongly. This is not because they do not exist. Loescher[23] has shown that the empty cobalt acceptor in GaP is neither hydrogenic nor d^6, for example. The difficulty is one of interpretation of the experimental results. An orbital with large d- and bonding p-like components will interact strongly with lattice vibrations; also transitions within the configuration will be allowed. As a result the optical absorption spectrum will consist of strong broad bands, and photoconductivity measurements will be needed to disentangle transitions within the configuration from transitions between the impurity and the conduction or valence bands. Also the theoretical expressions for the energy levels contain more parameters than the three required for d^n configuration, so one rapidly reaches the stage at which one has more disposable parameters than pieces of experimental

TABLE 8. OBSERVED $3d^n$ CONFIGURATIONS

	ZnO	ZnS	ZnSe	ZnTe	CdS	CdSe	CdTe	GaP	GaAs
Sc $+ d^2$									
Sc $2+ d^1$									
Sc $3+ d^0$									
Ti $+ d^3$									
Ti $2+ d^2$			O						
Ti $3+ d^1$									
V $+ d^4$									
V $2+ d^3$			O						
V $3+ d^2$		O,R	O		O,R	O			
Cr $+ d^5$		R	R	R			R		
Cr $2+ d^4$			O,R		R			O	
Cr $3+ d^3$									
Mn $+ d^6$									
Mn $2+ d^5$	R	O,R	O,R	R	R	R	R	R	R
Mn $3+ d^4$									
Fe $+ d^7$		R		R					
Fe $2+ d^6$		O	O	O	O		O	O	O
Fe $3+ d^5$	R	R	R	R	R			R	R
Co $+ d^8$									
Co $2+ d^7$	O	O,R	O,R	O,R	O,R		O,R	O	O
Co $3+ d^6$									
Ni $+ d^9$									
Ni $2+ d^8$	O	O	O		O			O	
Ni $3+ d^7$	R	R							
Cu $+ d^{10}$									
Cu $2+ d^9$	O,R	O			O				
Cu $3+ d^8$									

The symbols O and R indicate that the configuration has been observed by
an optical method or by spin resonance, respectively. The charge states
given are those of the ionic convention for II-VI compounds.

information. Despite this, further work in the area would be desirable because of the probable importance of these systems in recombination processes.

F. Energy Levels

We saw in Section III that the position of an impurity energy level $E(n,n-1)$ with respect to the conduction band is defined as the energy required to take an electron from a configuration with n electrons and to place it at the bottom of the conduction band far from the impurity. (Any other reference level, such as the top of the valence band, could equally well be used.) We therefore have to find the difference of energy of the state with n electrons and the state with n-1 electrons.

It is possible to make some progress with this problem if the configurations involved are d^n and d^{n-1}, i.e. if ionization of the impurity simply changes the occupancy of the d-shell. Table 8 showed that such a model is justified at least for some $3d^n$ impurities in II-VI compounds. The method followed is an extension of that given by Griffith[4] in discussing the ionization potentials of free atoms.

The total energy of the d-shell may be divided into two terms. The first comes from the interaction of the d-shell with the nucleus, the central core, and the spherically symmetrical part of the crystal potential. The second comes from electron-electron interactions within the d-shell together with the interaction of the d-shell with the non-spherically symmetrical part of the crystal field.

Of these, the first term is by far the largest, and cannot be calculated to anything like the required accuracy, say ±0.05 eV, by present techniques. However the difference, $E(d^{n-1}) - E(d^n)$, due to this term, can be small. We make the approximation that it varies linearly with atomic number, i.e. we assume that in the absence of interactions of the second type the impurity ionization would increase linearly as we go through a transition metal series. The approximation is reasonable because the nuclear charge increases as the atomic number increases, so the electron binding energy increases. Then the impurity levels for transitions from say a neutral to a negatively charged state might look something like Fig. 15. We have no means of calculating where the levels are, but if we can find two of them experimentally we can find the rest by linear interpolation.
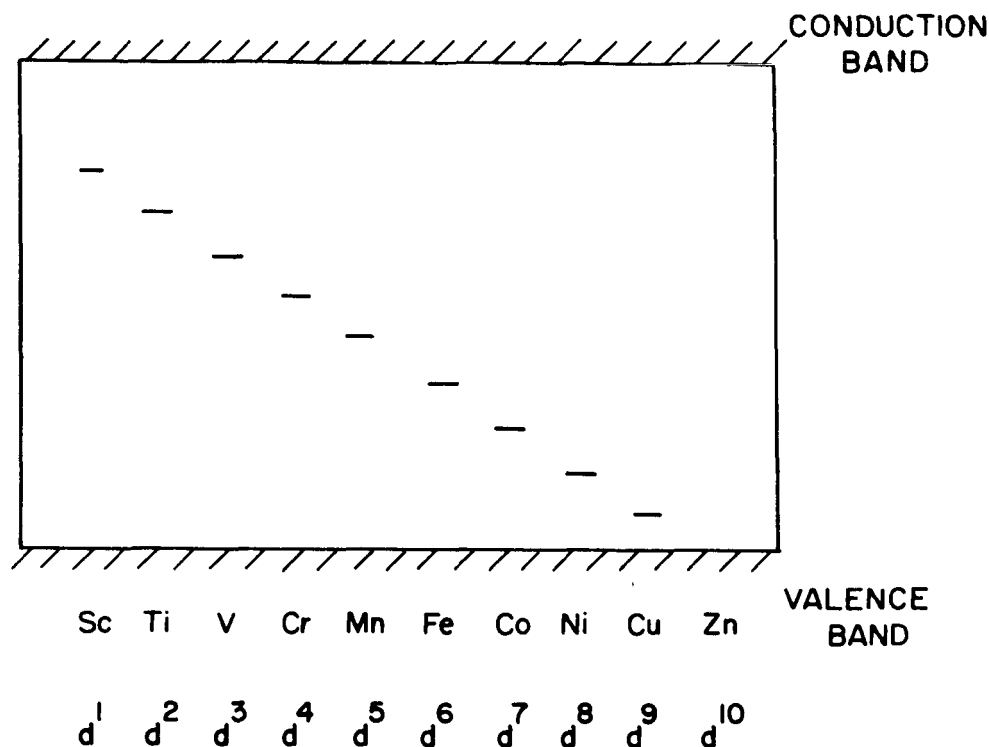
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FIG. 15. ENERGY LEVELS OF $3d^n$ IMPURITIES IN
ZnS IN THE LINEAR APPROXIMATION.

Next it is necessary to include terms of the second type, and these can be written down within the usual approximations of crystal field theory. Suitable tabulations can be found in a number of texts: one convenient source is Griffith.[4] As an example, the energies of the ground states of the d^6 and d^7 configurations, which would be appropriate to divalent and trivalent cobalt, are:

$$E(d^7) = 21A - 43B + 14C - \frac{6}{5} \triangle .$$ (13)

$$E(d^6) = 15A - 35B + 7C - \frac{3}{5} \triangle .$$ (14)

In these equations B, C and $\triangle$ are the usual Racah and crystal-field parameters, while A is a Racah parameter describing electrostatic interactions within the d-shell which shift the energy of the shell as a whole. Because $\triangle$ is small, Eqs. (13) and (14) are written in a linear approximation. Spin-orbit coupling terms have been omitted, because they are small in the $3d^n$ series (typically of the order of 0.05 eV), but they can easily be

included. The contribution to $E(d^{n-1}) - E(d^n)$ from terms in A varies linearly with n and so can be absorbed into the contribution from the spherically symmetrical interactions.

Using this semi-empirical approach, the problem is now solved in principle. The parameters B, C and $\triangle$ are to be found experimentally for each charge state of interest for each impurity, expressions for the configuration energies similar to Eqs. (13) and (14) are to be written down and their difference obtained, and a term is to be added which is linear in atomic number. The values of the linear term can be found if two of the ground-state energies within the transition metal series are known experimentally. Obviously such a procedure is hardly practicable unless a great amount of experimental information is available. By introducing further simplifying approximations it is possible to reduce the number of empirical parameters required ab initio to something more reasonable. The theory outlined above can then be used to predict ground-state energies and the methods described in earlier sections can be used to predict excited state energies. As further empirical parameters become known the theory can be refined as desired.

As a first approximation let us assume that B, C and $\triangle$ are the same for all $3d^n$ impurities in a given semiconductor. Inspection of Tables 2-5 shows that the approximation is crude but not outrageously so. Then the energy differences $E(d^{n-1}) - E(d^n)$ which give the position of the filled d^n level below the conduction band are given in Table 9. In this table terms in $\varphi + (n - 1)\eta$ are the linear terms from the spherically symmetrical interaction.

Allen[24] has used this approximation to interpret some of the properties of $3d^n$ impurities in ZnS. Figure 16 shows the calculated energies of the levels which, when full, have the impurity in the divalent state. To perform the calculations the values B = 550 cm^{-1}, C = 2600 cm^{-1} and $\triangle$ = 5000 cm^{-1} were used. The iron level was taken to be 1.4 eV below the conduction band, from measurements of photoexcited spin resonance by Rauber, Schneider and Matossi.[25] This fixes the value of $\varphi_1 + 5\eta$. To determine φ_1 and η separately some other piece of information is required, but unfortunately no other relevant precise measurements are available. However, if η is taken to lie between 4000 and 5000 cm^{-1} then energy levels

are obtained which are in reasonable accord with the known qualitative behavior of the impurities. The vertical bars of Fig. 16 show the calculated range of energy for this range of η.

$$d^1 \quad d^2 \quad d^3 \quad d^4 \quad d^5 \quad d^6 \quad d^7 \quad d^8 \quad d^9 \quad d^{10}$$

$$Sc \quad Ti \quad V \quad Cr \quad Mn \quad Fe \quad Co \quad Ni \quad Cu \quad Zn$$
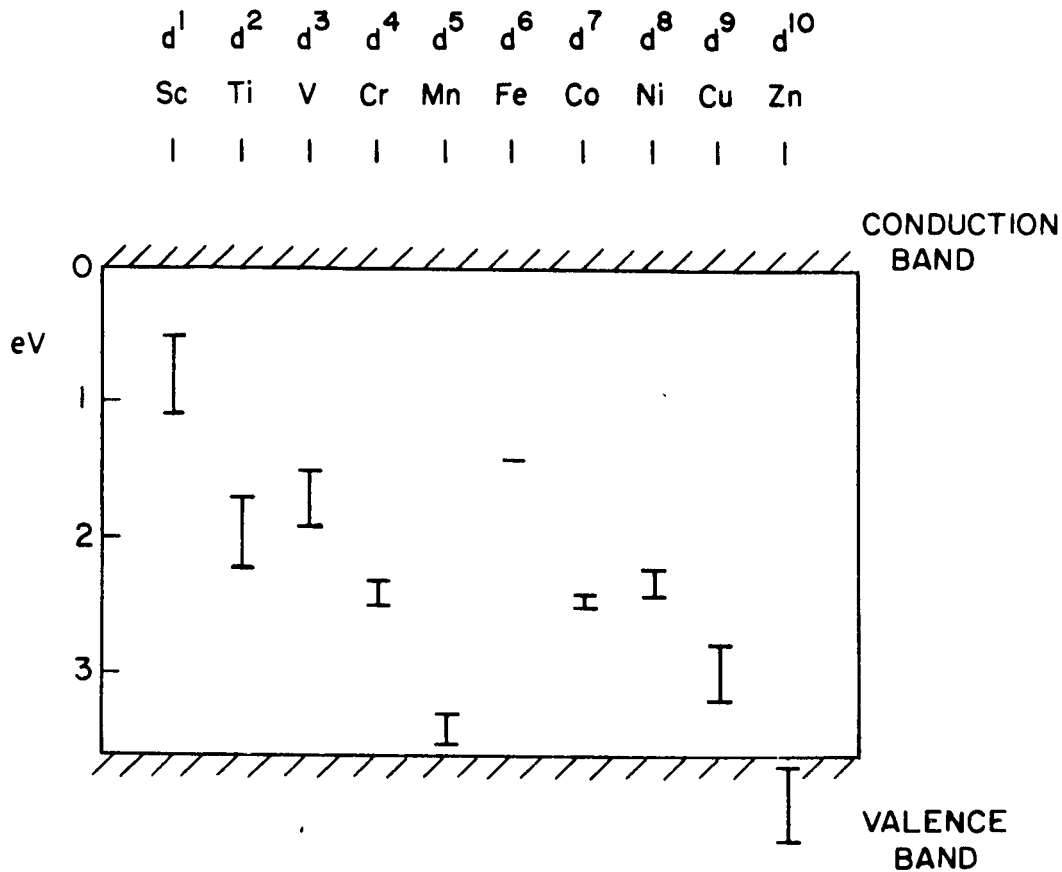
FIG. 16.   CALCULATED POSITIONS OF THE ENERGY LEVELS
OF DIVALENT TRANSITION METAL IONS IN ZnS.

The energy levels of several transition metal impurities in GaAs are known, particularly through the Hall effect measurements of Haisty and Cronin.[26]   If we assume that:

a)   the bonding orbitals are always filled, so the energy levels are associated with changes in the d-shell occupancy,

b)   the impurities are substitutional and isolated,

c)   the energy levels all correspond to the same charge states, namely $M^0 \rightarrow M^-$,

then it is possible to apply our theory. So far none of these assumptions have experimental justification, other than that the impurities appear to be acceptors. Using the methods of Section VI.C, we find from the refractive index that for cobalt and nickel $\beta \simeq 0.32$, giving $B = 330$ cm^{-1} and $C = 1550$ cm^{-1}, while for a III-V compound a mean value for $\triangle$ of 5000 cm^{-1} should be roughly right. We use these values for the whole $3d^n$ series. Fitting the expressions of Table 9 to the experimental ionization energies for vanadium and cobalt gives $\varphi_1 = -4540$ cm^{-1}, $\eta = 3450$ cm^{-1}.

TABLE 9. ENERGY DIFFERENCES BETWEEN THE d^{n-1}
AND d^n CONFIGURATIONS IN THE APPROXIMATION
THAT THE CRYSTAL FIELD PARAMETERS ARE
CONSTANT

n	$E(d^{n-1}) - E(d^n)$
1	$\varphi_1 + \frac{3}{5}\triangle$
2	$\varphi_1 + \eta + 8B + \frac{3}{5}\triangle$
3	$\varphi_1 + 2\eta + 7B - \frac{3}{5}\triangle$
4	$\varphi_1 + 3\eta + 6B - \frac{1}{5}\triangle$
5	$\varphi_1 + 4\eta + 14B - \frac{2}{5}\triangle$
6	$\varphi_1 + 5\eta - 7C + \frac{3}{5}\triangle$
7	$\varphi_1 + 6\eta - 7C + 8B + \frac{3}{5}\triangle$
8	$\varphi_1 + 7\eta - 7C + 7B - \frac{3}{5}\triangle$
9	$\varphi_1 + 8\eta - 7C + 6B - \frac{1}{5}\triangle$
10	$\varphi_1 + 9\eta - 7C + 14B - \frac{2}{5}\triangle$

Table 10 gives the resulting ionization energies, together with the observed ones. For chromium and nickel the calculated value lies within the spread of experimental values. Iron and copper appear to associate with other impurities, so it is not surprising that there is no agreement between the calculated and experimental values. For manganese the

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TABLE 10. EXPERIMENTAL AND THEORETICAL IONIZATION ENERGIES
OF TRANSITION METAL IMPURITIES IN GaAs.

	$E_c - E_I$ Theory	$E_c - E_I$ Expt.[*]	$E_I - E_v$ Expt.[*]	Ref.
Sc	-0.19 eV			
Ti	0.56			
V	0.21	0.21 eV		1
Cr	0.84	0.73		1,2
Mn	1.47	1.41		3
Fe	0.60	1.00	0.52 eV	1
"		1.15	0.37	4
Co	1.36	1.36	0.16	1
Ni	1.00	0.99	0.53	7
Cu	1.63		0.023, 0.15	5
Zn	2.26		0.04	6

[*]Extrapolated to 0°K, and assuming E_g = 1.52 eV.

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agreement is good but it must be acknowledged that this is partly coincidental. In tetrahedral coordination the Racah parameters appear to be reduced less for manganese than for cobalt. The correct value of $E_c - E_I$ will therefore be a little greater than 1.47 eV, so the manganese level lies just below the top of the valence band. (The same argument may well apply to ZnS:Mn.) This means that the energy required to remove an electron from the d-shell is greater than the energy required to remove an electron from the bonding orbitals. Manganese is therefore a hydrogen-like acceptor, but the nearness of the d-shell level leads to an appreciable amount of configuration mixing. (Compare the 0.04 eV energy of the zinc acceptor, with negligible mixing, with the 0.11 eV energy for manganese.)

The argument just given is general. We find the energy of the lowest acceptor level, $E(M^- \rightarrow M^o)$, for the case in which all the bonding orbitals remain filled. If the level lies below the top of the valence band, it will be energetically favorable for an electron to fall from the bonding orbitals into the level. The acceptor will now be hydrogenic, with its level just above the valence band. Isolated substitutional manganese, copper and zinc in GaAs are in this category. In a similar manner we find that the lowest acceptor level of scandium lies above the bottom of the conduction band so it will normally be full. Scandium should therefore not act as an acceptor in GaAs. Since the acceptor level is degenerate with conduction band levels it will be a resonant one, and could contribute to the scattering of hot electrons.

In addition to the levels that we have calculated, there may be others corresponding to other charge states, e.g. $E(M^- - M^{2-})$. These can be found by the same procedure as above when sufficient data are available to estimate the parameters. Of course, finding the energy levels of different charge states and configurations with respect to the valence band is, in chemical terms, finding the possible valence states of the impurities. Sometimes the attempt has been made to reverse the procedure, i.e. to predict possible charge states from the commonly occurring valences in compounds. The approach can be fruitful in rather ionic semiconductors, but in the strongly covalent semiconductors the effect of screening decreases the energy separation between charge states, so more valences can occur than might be expected.

The method of calculation of energy levels that we have described is rather far from a first principles calculation. It has the disadvantage that it cannot be applied until some experimental data are available, but has the advantage of making good use of such data, and can be successively refined as more data are acquired. In this section only $3d^n$ impurities were discussed, but the method is applicable to other series, in particular the rare earths. For instance, in unpublished work we have been able to explain the frequent occurrence of divalent samarium, europium, thulium and ytterbium, while the rest of the series are normally trivalent.

G. Kinetics

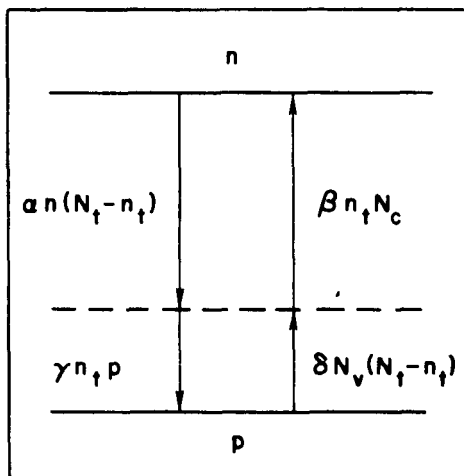Photoconductivity and luminescence are accompanied by changes in the populations of the various impurity levels present. Figure 17 illustrates the reactions occurring in the simplest possible case, that of a single impurity level. Because of the presence of nonlinear terms, such as $\gamma n_t p$, there is no simple general solution to the equations describing the kinetics of the system. (Simple approximate solutions, of which the Hall-Shockley-Read formula[27] for carrier lifetime is an example, can be found for special limiting cases, such as small concentration of recombination centers.) In addition, three parameters are needed to typify each level, namely the capture cross-sections for holes and electrons and the energy of the level. The four reaction constants of Fig. 17, α, β, γ and δ, may be expressed in terms of these parameters. When more than one level is present the situation is correspondingly more

FIG. 17. TRANSITIONS TO AND FROM A SINGLE IMPURITY LEVEL.

n   conc. of free electrons

p   conc. of free holes

N_t conc. of impurities

n_t conc. of electrons on impurities

N_c conduction band density of states

N_v valence band density of states

complex. As a result, it is nearly always possible to set up a model which will explain any given set of experimental data on, say, variation of photoconductivity with light intensity, and to deduce values of the parameters. It is hardly ever possible to show that the model is either unique or correct. In this connection M. Maurice Bernard[28] has made the comment "Concerning the value of capture cross-sections one must observe, when several pieces of information are available, a general disagreement."

Clearly a method of measuring some of the quantities involved in the kinetic processes would be valuable in sorting out what is going on. Hall effect measurements on illuminated samples can give information concerning the free carriers, as Bube and his co-workers have shown. Measurements of optical absorption, luminescence or spin resonance can give corresponding information concerning the occupancies of impurity levels. The principle is well known. As examples, Schon[29] has used simultaneous measurements of photoconductivity and luminescence to elucidate some processes in ZnS. Schneider and his associates[30] have demonstrated by spin resonance that $Fe(d^6)$ in ZnS can trap both holes and electrons, becoming d^5 or d^7. Gumlich and Schulz observed a change in the number of $Co(d^7)$ centers in ZnS on illumination. Numerous similar studies have been reported. However all of these have been concerned with one or other partial aspect of the problem: as yet there is still no reasonably complete investigation of a photoconductive process in which a deep level is involved.

H.   Photo-ionization Spectra

Photoconductivity and certain types of luminescence involve optical transitions in which an electron goes from an impurity to a conduction or valence band. Despite the technical importance of these subjects, there exists as yet no theory of, say, the excitation spectrum or the strength of the transition. Using the model of transition metal impurities developed in previous sections, it is possible to lay the groundwork of such a theory.

Consider a transition in which the impurity has a configuration d^n in the initial state and d^{n-1} in the final state. (The theory also holds for f^n configurations.) The electric dipole is represented by a one-electron operator so there is a selection rule that the transition matrix

elements will involve only single orbital changes. We therefore need only consider terms of the type

$$\langle d^n \, S\Gamma \, | \, \underset{\sim}{r} \, | \, d^{n-1} \, S'\Gamma'\varphi \rangle , \tag{15}$$

where S, Γ are spin and symmetry labels and φ is a valence band or conduction band state. It is possible to uncouple a d-orbital from the d^n configuration by using the idea of fractional parentage. The state d^n is expressed as a combination of a d^{n-1} state with a d state, summed over the allowed values of S, Γ. Tabulations of the relevant coefficients are given for example by Griffith[4] or by Nielson and Koster.[31] By this means the elements of Eq. (15) can be reduced to terms of the form

$$\langle d \, | \, \underset{\sim}{r} \, | \, \varphi \rangle . \tag{16}$$

To illustrate the behavior of these terms we consider a tight-binding model of a semiconductor with band extrema at the center of the Brillouin zone, as in the II-VI or some III-V compounds. In these the top of the valence band is made up predominantly of atomic p-orbitals and the matrix elements (16) correspond to allowed transitions. The optical spectrum will reflect the density of states and will have the form

$$\begin{matrix} (\nu - \nu_o)^{1/2} & \quad \nu > \nu_o \\ \\ 0 & \quad \nu < \nu_o \end{matrix} \tag{17}$$

where $h\nu_o$ is the energy of impurity from the valence band. At higher energies the absorption will contain extra terms corresponding to the impurity ending in an excited state.

The conduction band of these compounds is made up of s-orbitals near the minimum so transitions are parity-forbidden. Two effects then come into play. As one goes up the conduction band p-like behavior occurs and there will be a gradually increasing contribution to the intensity as energy increases. In addition, if the lattice site of the impurity lack inversion symmetry, as in the zinc-blende or wurtzite structures, then parity will not be a good quantum number for the impurity orbitals. The

p-orbitals at the top of the valence band have t_2 symmetry and can mix with the t_2 d-orbitals, giving states of the form

$$\cos\theta \; |t_2(d)\rangle + \sin\theta \; |t_2(p)\rangle, \qquad (18)$$

where θ is a small angle. The odd parity part will then have a non-zero interaction with the s-like conduction band. In order to evaluate this contribution it is necessary to estimate θ, which may be done in principle by using the measured oscillator strengths for transitions with the d-shell.

Actual calculations have not yet been performed, but one can see the qualitative results. Optical transitions from the valence band of a II-VI or III-V semiconductor to a transition metal impurity will be strong and have a simple spectrum with a reasonably well-defined threshold corresponding to the energy level of the impurity. Transitions to the conduction band will have a form which consists of the addition of a number of terms and will be weak in the threshold region. Empirical extrapolation to a threshold energy in order to obtain the impurity energy level may be an unreliable procedure.

VII. CONCLUSIONS

Experimentally we find that crystal field theory is useful even for strongly covalent materials like gallium phosphide. The parameters appearing in the theory cannot, at this stage, be calculated from first principles but have to be treated as empirical quantities. In the II-VI and III-V compound semiconductors the values of the parameters show certain regularities of behavior, so that when they are known for a few compounds they can be estimated for other members of the series. This fact gives the theory a predictive character which enhances its usefulness.

At its simplest, the theory can be used to determine the charge state and position in the lattice of transition metal or rare earth impurities. Variations in the charge state with position of the Fermi level can often be monitored in this way. Electron spin resonance and optical absorption are two experimental techniques available for the purpose. They are to some extent complementary: optical absorption is rather simpler and, for many impurities, is more sensitive, while spin resonance can be used for some configurations which are difficult to detect optically, such as d^5, and can give more detailed information concerning the environment of the impurity.

The theory has been extended to account for the positions of the impurity levels with respect to the valence and conduction bands of the semiconductor. The properties of several of the $3d^n$ impurities in ZnS and GaAs have been explained in this way. Although the rare earth impurities have not been treated specifically in this report, some of their properties can be explained in the same manner. A further extension of the theory should give the absorption spectra for the excitation of a charge carrier from the impurity to the conduction or valence bands, and an outline of the method has been described. Since these are the transitions involved in impurity photoconductivity and luminescence, the matter is worth pursuing.

Molecular orbital and other more fundamental approaches have not reached the stage at which they can give an adequate general description of the properties of impurities in semiconductors. The experimental data indicate some of the factors which must be incorporated into any

theory. In the II-VI and III-V compounds the major effect is the reduction of the Racah parameters from their free ion values. The reduction factor β can be as small as 0.3. Similarly the interaction of the d-electrons with the nucleus and core shell is much reduced. In ZnS an increase of the nuclear charge by one unit increases the binding energy of a d-electron by about 4000 cm^{-1}, while for a free ion the increase is about 15000 cm^{-1}. The Racah parameter reduction varies from semiconductor to semiconductor and is correlated with the polarizability of the bonding electrons, which suggests that it is primarily a screening effect. On the other hand the value of the crystal field parameter $\triangle$ appears to be a characteristic of the impurity rather than the host. Baranowski et al[32] find that for $Fe(d^6)$ the value of $\triangle$ varies through the series ZnS, ZnSe, ZnTe, but only by 20%. From this it would seem that the major contribution to $\triangle$ is from the bonding electrons centered on the impurity itself.

It will be obvious from the discussion that we are describing the early explorations of a new field as far as semiconductors are concerned, rather than reviewing the achievements of a completed investigation. Very little is known concerning deep-lying impurities in semiconductors: we hope that this report shows that some progress is possible and is being made.

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