

Crystal-Field Spectra of $3d^n$ Impurities in II-VI and III-V Compound Semiconductors*

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(Received 14 March 1967)

The spectra of Fe(d^6) in ZnSe, ZnTe, CdS, CdTe, GaP, and GaAs, and of Co(d^7) in ZnSe, ZnTe, CdTe, GaP, and GaAs, are presented. It is found that a crystal-field description is useful even in such covalent materials. The crystal-field splitting Δ depends on the impurity, but for a given impurity, Δ varies by less than 25% through the II-VI series. The Racah parameter B is strongly dependent on the host crystal and can decrease to less than a third of the free-ion value. From plots of the variation of B and Δ with properties of the impurity or host crystal, the spectra of hitherto unexplored systems may be predicted.

I. INTRODUCTION

IN recent years a number of studies have been made of the optical absorption spectra of $3d^n$ transition-metal impurities in II-VI semiconductors. Examples are the work of Pappalardo and Dietz¹ with CsS, and of Weakliem² with ZnO, ZnS, and CdS. Loescher *et al.*³ extended the area to the III-V semiconductors by investigating Co(d^7) in GaP. It is found that the spectra are well described by crystal-field theory as long as the Racah parameters B and C and the crystal-field splitting Δ are taken as quantities to be determined by experiment. There is as yet no theoretical justification for this fact.⁴ A point-charge model for the lattice is clearly inapplicable, and molecular-orbital calculations have not yet reached the stage at which they can do more than qualitatively reproduce some experimental observations, when the host lattice is as strongly covalent as the ones under consideration.

To elucidate some of the operative mechanisms, we have investigated the way in which the parameters B and Δ vary with impurity and with host lattice. Iron (d^6) and cobalt (d^7) were chosen for particular attention. They are easily introduced into the appropriate lattices. Iron (d^6) in tetrahedral coordination has a first-excited level whose position is independent of B , so information on the variation of Δ is simply obtained. Cobalt (d^7) has a distinctive spectrum in a convenient spectral range, from which both Δ and B may be obtained.

II. EXPERIMENTAL

The II-VI and III-V semiconductors were in the form of solid ingots which were either single crystal or

coarsely polycrystalline. Iron or cobalt were normally introduced by evaporating a layer of metal onto a slice of semiconductor and then diffusing at high temperature. The ZnSe:Co samples were grown by Dr. S. J. Bass of Services Electronics Research Laboratory by melting ZnSe in a closed ampoule in the presence of cobalt oxide. The ZnSe:Fe samples were also grown by Dr. Bass, using vapor transport in a closed tube with a trace of halide as transporting agent. (Without the halide the ZnSe transports, but not the iron.) After polishing, the samples were mounted on the cold-finger of a Dewar which had sapphire windows. A carbon resistance thermometer was used to monitor the sample temperature. Because of the low thermal conductivity of materials containing Fe(d^6), discovered by Slack,⁵ it was found that samples nominally at liquid-helium temperatures were in fact at temperatures ranging up to 8°K. Spectra were measured on a Cary 14 IR spectrophotometer out to $2.5\ \mu$ ($4000\ \text{cm}^{-1}$) and on a Perkin-Elmer 621 spectrophotometer for longer wavelengths.

From arguments similar to those used by Loescher *et al.*³ for GaP:Co, it appears that the spectra are due to iron or cobalt on substitutional cation sites.

III. EXPERIMENTAL RESULTS

A. Iron (d^6)

The spectra of Fe(d^6) in the zinc-blende crystals ZnSe, ZnTe, CdTe, GaP, and GaAs, and in the wurtzite crystal CdS, are shown in Fig. 1. There are a few closely-spaced zero-phonon lines at low energies with widths less than the resolution used, namely, $6\ \text{cm}^{-1}$. At higher energies there is a broader, more complex structure. Slack *et al.*⁶ have found similar spectra for iron in cubic ZnS and CdTe.

Low and Weger⁷ have given expressions for the crystal-field levels of a d^6 configuration in a cubic field, with spin-orbit interactions included. In a tetrahedral field the 5D term is split into the levels shown in

* Work supported by the National Aeronautics and Space Administration Grant No. Nsg-555 and by the Advanced Research Projects Agency.

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¹ R. Pappalardo and R. E. Dietz, *Phys. Rev.* **123**, 1188 (1961).

² H. A. Weakliem, *J. Chem. Phys.* **36**, 2117 (1962).

³ D. H. Loescher, J. W. Allen, and G. L. Pearson, *J. Phys. Soc. Japan Suppl.* **21**, 239 (1966).

⁴ J. S. Griffith, *J. Chem. Phys.* **41**, 576 (1964).

⁵ G. A. Slack and S. Galginitis, *Phys. Rev.* **133**, A253 (1964).

⁶ G. A. Slack, F. S. Ham, and R. M. Chrenko, *Phys. Rev.* **152**, 376 (1966).

⁷ W. Low and M. Weger, *Phys. Rev.* **118**, 1119 (1960).

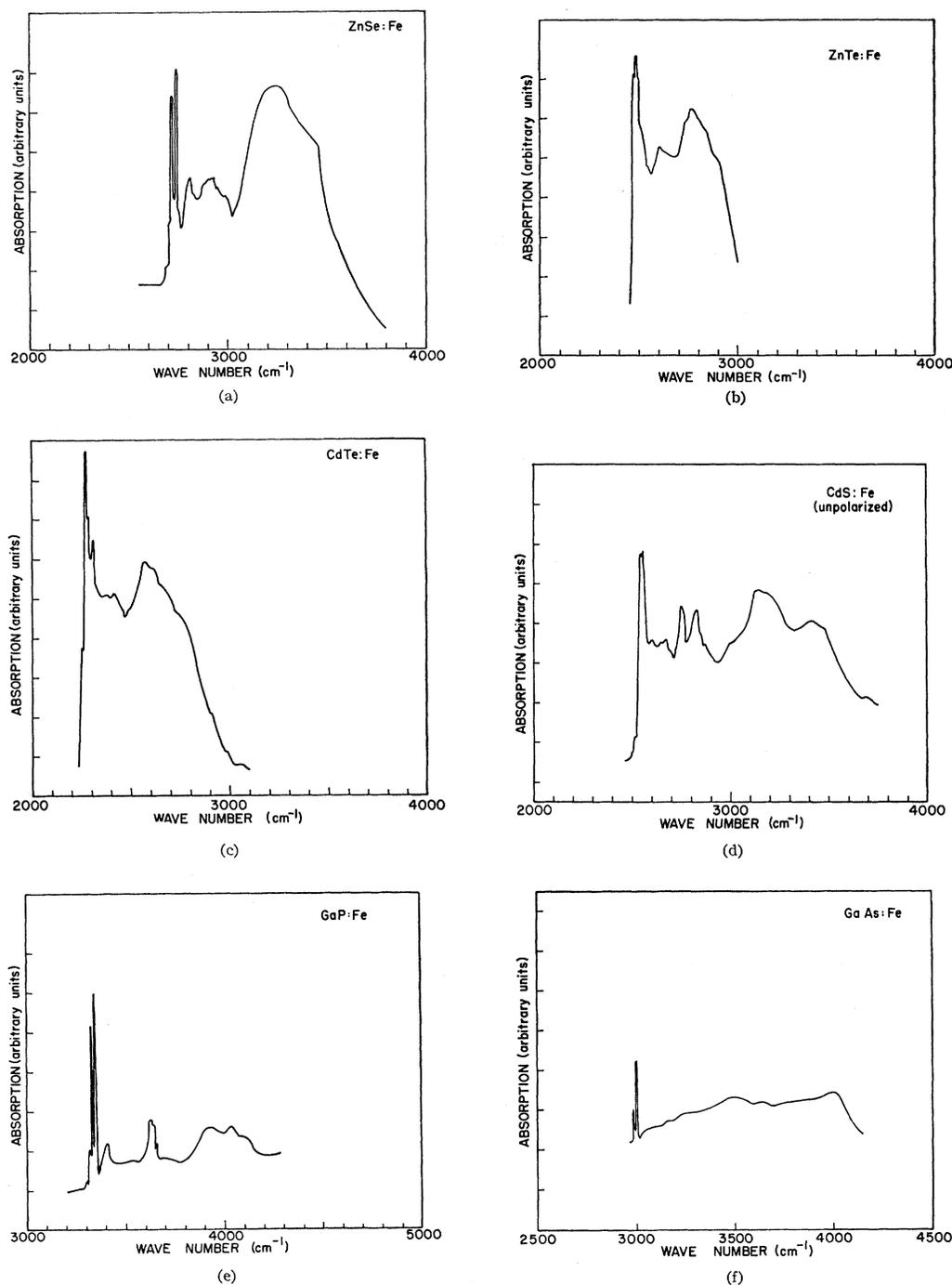


Fig. 1. Spectra of $\text{Fe}(d^6)$ at liquid-helium temperature in tetrahedrally-coordinated semiconducting compounds.

Table I, in which the energies are given to second order. We interpret the sharp lines as being transitions from the 5E levels to the lowest level of 5T_2 , the decrease of intensity with decrease in energy reflecting the Boltzmann distribution over the levels. Table II gives the position of the strongest sharp line, the separation of the lower energy from it, and a calculated set of separa-

tions taking as representative values $\Delta = 2700 \text{ cm}^{-1}$ and $\lambda = -80 \text{ cm}^{-1}$. (The free-ion value is -103 cm^{-1} .) There appears to be no static Jahn-Teller effect, for otherwise we should have a different line pattern, as may be seen from the calculations of Low and Weger. Goodenough⁸

⁸ J. B. Goodenough, J. Phys. Chem. Solids 25, 151 (1964).

TABLE I. Energy levels to second order of d^6 in a tetrahedral field. Δ =crystal-field splitting, λ =spin-orbit coupling parameter.

5T_2	$\Delta - 2\lambda + 24\lambda^2/\Delta$
	$\Delta - 2\lambda + 12\lambda^2/\Delta$
	$\Delta - 2\lambda + (12/5)\lambda^2/\Delta$
	$\Delta + \lambda + 12\lambda^2/\Delta$
	$\Delta + \lambda + 6\lambda^2/\Delta$
	$\Delta + 3\lambda + (18/5)\lambda^2/\Delta$
5E	0
	$-6\lambda^2/\Delta$
	$-12\lambda^2/\Delta$
	$-18\lambda^2/\Delta$
	$-24\lambda^2/\Delta$

has given arguments to show that static Jahn-Teller distortions of tetrahedral $\text{Fe}(d^6)$ in moderately covalent hosts should be small, in agreement with our observations.

The structure at higher energies is harder to interpret, partly because it is difficult to distinguish between vibronic and electronic transitions. From Table I it is seen that there should be two lines at $2|\lambda|$ and $5|\lambda|$ beyond the sharp lines, each split by second-order interactions. If the two broad structured bands in the spectra are attributed to these transitions, then the value of λ varies strongly from host to host, ranging down to half the free-ion value. This is in contradiction to the splitting of the ground state. A possible explanation lies in the Ham effect,⁹ in which dynamical Jahn-Teller distortions reduce the apparent value of some first-order splittings, but may not effect second-order interactions. Unfortunately, we have no way of estimating the magnitude of the effect. Indeed, the apparent reduction of λ may be so great that the transitions to the 5T_2 levels are all contained in the structure close to the main sharp line.⁶ Since the fine structure is not the primary concern of this paper, we simply note that the main sharp line will have an energy

$$E = \Delta + 3\gamma\lambda + \frac{138}{5} \frac{\lambda^2}{\Delta}, \quad (1)$$

where γ is a reduction factor lying between 0 and 1.

In the wurtzite structure, the cation site has approxi-

TABLE II. Position of the main sharp line in $\text{Fe}(d^6)$ absorption spectra at liquid-helium temperature, and energy separation of lower-energy lines from the main line. Calculated values for $\Delta=2700$, $\lambda=-80$. All energies in cm^{-1} .

	ZnS ^a	ZnSe	ZnTe	CdTe	GaP	GaAs	
Main line (cm^{-1})	2947	2738	2486	2282	3344	3002	Calc.
Separation	1	0	0	0	0	0	0
	2	15	17	15	13	14	14
	3	26	28	...	24	...	28
	4	46	43	...	39	...	43

^a Reference 6.

⁹ F. S. Ham, Phys. Rev. **138**, A1727 (1965).

mate tetrahedral symmetry, together with a small axial component. Correspondingly, the spectrum of CdS:Fe is similar to that of the zinc-blende materials but shows small additional splitting. Four lines are resolved, and from these we deduce $\Delta=2800 \text{ cm}^{-1}$, $\lambda=-95 \text{ cm}^{-1}$, and the trigonal axial field component b is $+70 \text{ cm}^{-1}$.

B. Cobalt(d^7)

Pappalardo and Dietz¹ have discussed in detail the fitting of the spectrum of CdS:Co to a crystal-field level scheme, and Weaklien² has done the same for ZnO:Co , ZnS:Co , and CdS:Co . We find similar spectra for $\text{Co}(d^7)$ in ZnSe , ZnTe , and CdTe , as shown in Fig. 2. Just beyond the visible region there is a strong peak due to the ${}^4A_2(F)-{}^4T_1(P)$ transition, showing structure caused by spin-orbit splitting and mixing with nearby doublets. Further into the infrared there is another absorption due to the ${}^4A_2(F)-{}^4T_1(F)$ transition, and near 3500 cm^{-1} is the very weak absorption due to the symmetry-forbidden ${}^4A_2(F)-{}^4T_2(F)$ transition. Table III¹⁰ gives the values of B and Δ as deduced from the spectra.

TABLE III. Crystal-field parameters for $\text{Co}(d^7)$ in zinc-blende and wurtzite semiconductors.

Host	B (cm^{-1})	Δ (cm^{-1})	Ref.
ZnO	775	3900	2
ZnO	700	3900	10
ZnS	610	3550	2
ZnSe	570	3800	
ZnTe	460	3450	
CdS	610	3300	2
CdS	664	3160	1
CdTe	485	3150	
GaP	290	5400	3

Loescher *et al.*³ measured the spectrum of GaP:Co at liquid-nitrogen temperature and deduced values for B and Δ . At helium temperatures, the spectrum, Fig. 2(d), is better resolved. It is not possible to fit the absorption peaks exactly with crystal-field expressions, but the values $B=290 \text{ cm}^{-1}$, $\Delta=5400 \text{ cm}^{-1}$, give a fit to within 200 cm^{-1} . In GaAs:Co the breakdown of the crystal-field approach has gone further. The distinctive ${}^4T_1(P)$ absorption is clearly visible in Fig. 2(e), even though it is close to the main absorption edge of GaAs . Three other bands are seen. Without additional experiments it is not possible to identify them, since ${}^4T_1(F)$ will be interacting with nearby doublets. No set of values of B , Δ , and λ fit the spectrum exactly, but it appears that Δ is about the same as for GaP:Co , while B must be less than a quarter of the free-ion value.

¹⁰ R. Pappalardo, D. L. Wood, and R. C. Linares, J. Chem. Phys. **35**, 2041 (1961).

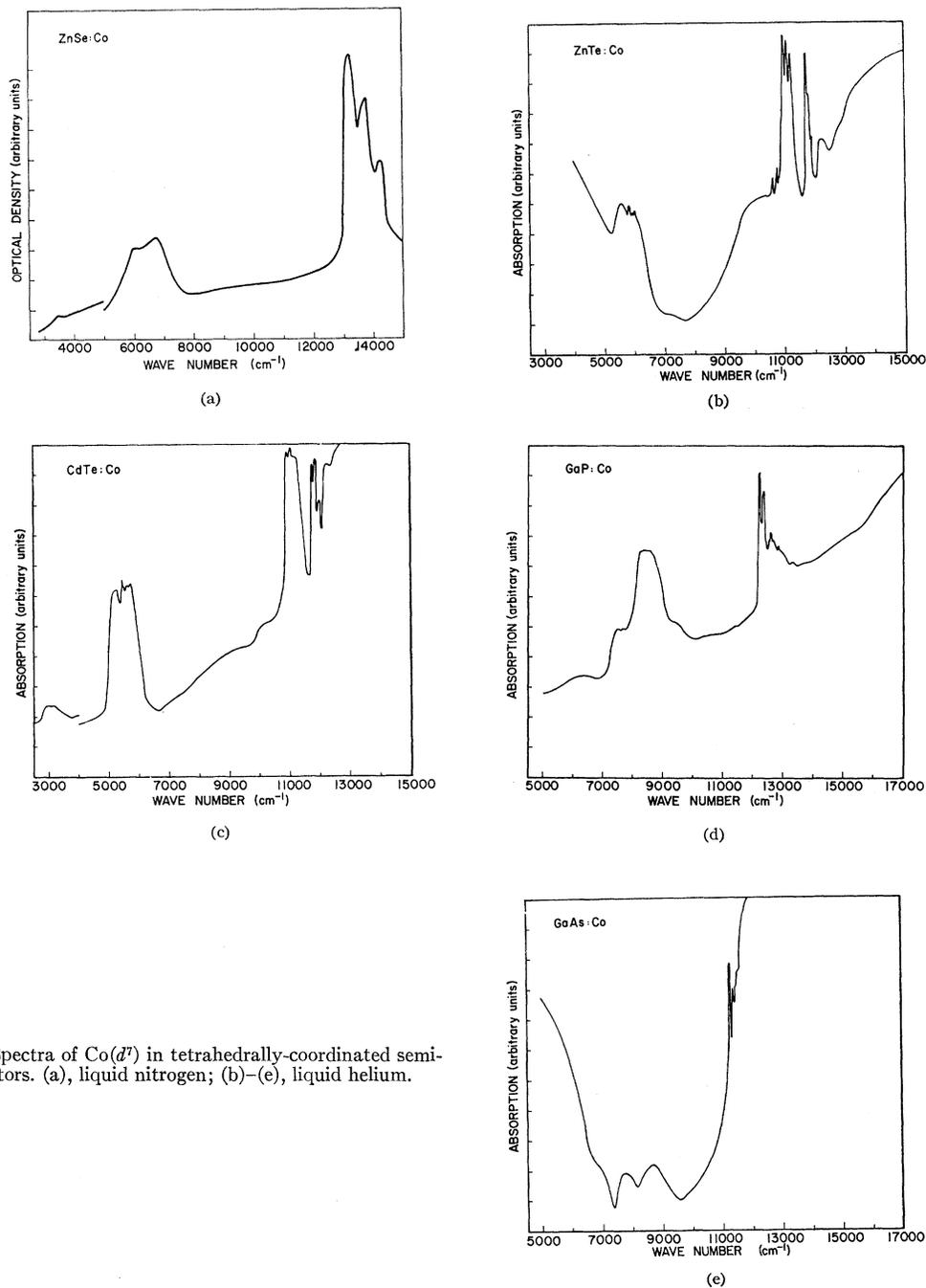


FIG. 2. Spectra of $\text{Co}(d^7)$ in tetrahedrally-coordinated semiconductors. (a), liquid nitrogen; (b)–(e), liquid helium.

IV. DISCUSSION

It may be seen from Eq. (1) that for $\text{Fe}(d^6)$, the value of Δ is close to the energy of the main sharp line. Figure 3 shows the main line energy in II–VI compounds as a function of atomic spacing in the host lattice. The variation in energy is not great, but there is a definite trend for Δ to decrease as the crystal spacing increases and the crystal becomes more covalently bonded. In gallium phosphide, iron with a d^6 configuration has

accepted an electron and is negatively charged with respect to the gallium atom that it replaces. The value of Δ for GaP:Fe is 15% greater than it would be for a II–VI compound with the same lattice constant, while for GaAs:Fe the corresponding figure is 8%.

Inspection of Table III shows that, for $\text{Co}(d^7)$ in the II–VI series, the variation of Δ is again rather small. Any systematic variation is largely masked by uncertainties in the parameter values, but again Δ tends

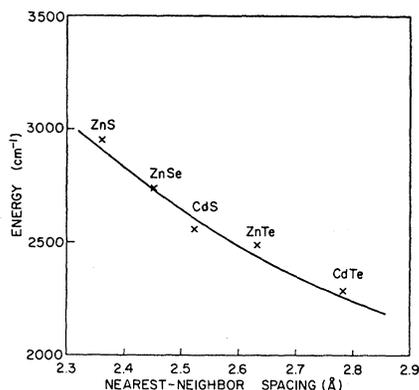


FIG. 3. Variation of the position of the strongest sharp line in the spectrum of $Fe(d^6)$ with atom spacing of the host crystal.

to decrease as the crystal becomes more covalent. Cobalt (d^7) in GaP is negatively charged and the value of Δ is again increased over that expected for a corresponding II-VI compound, this time by about 50%.

Since Δ is roughly constant for a given $3d^n$ impurity in the II-VI series, it is meaningful to ask how Δ varies with impurity, irrespective of the host crystal. Before doing so, we have to consider one complication. When comparing electronic transition energies, one should use the barycenters of the absorption bands,¹¹ not the zero-phonon line positions. In the semiconductors

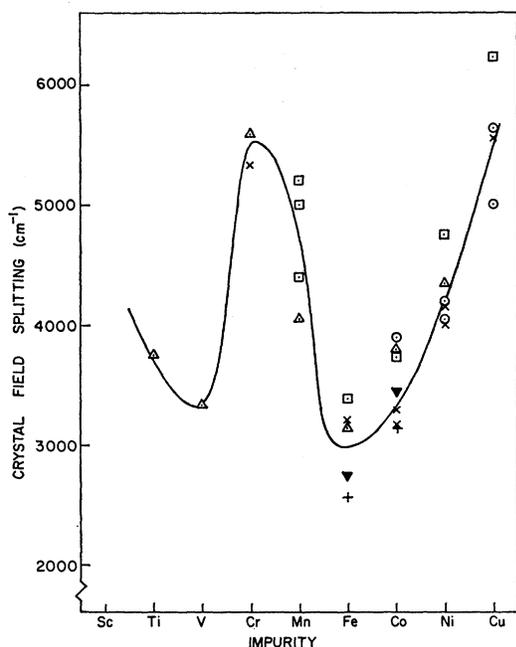


FIG. 4. Variation of the crystal-field splitting Δ through the first transition series for impurities in II-VI semiconductors. \circ , ZnO; ∇ , ZnTe; \square , ZnS; \times , CdS; \triangle , ZnSe; $+$, CdTe.

¹¹ M. H. L. Pryce and W. A. Runciman, *Discussions Faraday Soc.* **26**, 34 (1958), D. E. McCumber, *Phys. Rev.* **135**, A1676 (1964).

discussed in this paper, the distinction is unimportant except for manganese (d^5) and iron (d^6). The values of Δ for $Fe(d^6)$ used here are therefore greater by about 200 cm^{-1} than those used above. Figure 4 shows Δ for divalent transition metal impurities in II-VI compounds. The data were in part culled from the literature, while other points came from the present work and form the unpublished absorption spectra measured by one of us (JWA) for $Ti(d^2)$, $V(d^3)$, $Cr(d^4)$, and $Ni(d^8)$ in ZnSe. Because of special difficulties of interpretation, the values for $Mn(d^5)$ are open to question. It can be seen that the data exhibit a definite pattern, with Δ being greatest near filled or half-filled shells. We have no explanation for this. Slack⁵ has observed a superficially similar behavior of the covalent radii of the divalent atoms, but the maxima and minima in the radii occur at one atomic number greater than the corresponding feature in Δ .

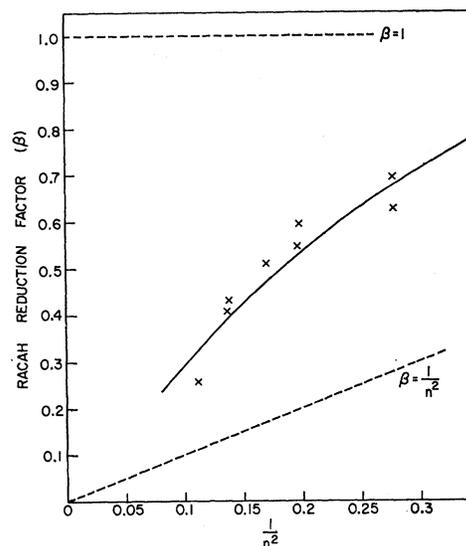


FIG. 5. Variation of the Racah parameter reduction factor β with n^{-2} , where n is the infrared refractive index, for $Co(d^7)$.

Weakliem² has pointed out a correlation between the Racah parameter B and the anion polarizability for $Co(d^7)$ in various compounds. Our results enable this to be extended to much lower values of B . Because we are also interested in III-V compounds, it is more convenient to use the electronic dielectric constant (i.e., n^2 , the square of the infrared refraction index), as being more accessible than the anion polarizability. Figure 5 shows the relation between n^{-2} and β , where β is the ratio of the value of B in the crystal to that in the free ion. A simple correlation exists. It is interesting to note that the point for GaP is not far from the line for the II-VI compounds. The correlation is intelligible if the reduction of B is due to screening of d -orbital electrostatic interactions by the bonding electrons. If, as a consequence of the screening, the d orbitals were expanded

over many lattice sites (an extreme case not realized in practice, of course), then they would feel the full dielectric screening and β would be equal to n^{-2} . If the screening were small, then the d orbitals would behave much as if they were in a free ion, and β would become unity. In accordance with this idea, at large n the line of Fig. 5 approaches the line $\beta=n^{-2}$, and at small n it approaches the line $\beta=1$.

The value of β for Ni(d^8) behaves similarly. There is as yet insufficient evidence to discuss the variation of β in other configurations.

V. CONCLUSIONS

It is clear from the discussion that there are two quite separate effects on d -orbital energies when a $3d^n$ impurity is placed substitutionally in II-VI or III-V semiconductors. The first is a reduction of the electrostatic interactions, and the second is a splitting of the d levels by the tetrahedral environment. It is also clear that the reduction of B is at least as important as the splitting Δ , in governing transition energies. Any theory which attempts to explain the magnitude of Δ but which ignores, or fails to explain, the magnitude of β must be of very limited validity for the materials discussed here. Experimentally, the value of β is found to be strongly dependent on the host crystal, while Δ is mainly a function of the impurity itself. There is no direct correlation between the two, although broadly speaking both β and Δ decrease as the crystal becomes more covalent.

It may well be that the use of a crystal-field description will turn out to be an equivalent representation of the real, complicated situation, in the same sense that the use of operator equivalents can simplify a more complicated problem.⁴ Many of the effects of covalency are then taken into account by using empirical values of B and Δ . The calculation of ground-state energies of

impurities relative to the conduction or valence band of the host crystal¹² was carried through in this spirit. The importance of the reduction of the electrostatic parameters is apparent when this calculation is performed for ZnS and for GaAs. Energy level differences of the order of 1 eV arise from differences of B , whereas differences of Δ only contribute of the order of 0.1 eV. Our results suggest that other calculations, such as those of Powell *et al.*¹³ on the higher-order splitting of 6A_1 in Mn(d^5), might give closer agreement with experiment for covalently bonded materials if, instead of taking B as constant and Δ as variable, one takes Δ as constant and B as variable.

Finally, two practical points emerge. First, a crystal-field description in which the parameters are empirical is useful even for materials as covalent as GaP or CdTe, although it is beginning to break down for GaAs. Second, the values of the parameters can often be estimated by means of the correlations given here, a result which is of considerable use in interpreting spectra.

ACKNOWLEDGMENTS

We are grateful to the various people who kindly supplied us with materials, particularly Dr. S. J. Bass, of Services Electronics Research Laboratory, England and Professor D. A. Stevenson of the Department of Materials Science at Stanford University. We are also grateful to Dr. G. A. Slack of the G. E. Research Laboratory for communicating his results to us before publication.

¹² J. W. Allen, *Proceedings of the International Conference on Semiconductors, Paris 1964* (Dunod Cie, Paris, 1964), p. 781.

¹³ M. J. D. Powell, J. R. Gabriel, and D. F. Johnston, *Phys. Rev. Letters* **5**, 145 (1960).