

Electron Paramagnetic Resonance of Photosensitive Iron Transition Group Impurities in ZnS and ZnO

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The photosensitive iron transition group impurities Fe, Ni, and V in cubic ZnS and Ni in ZnO have been studied by electron paramagnetic resonance. The charge states Fe^{2+} , Fe^+ , Ni^{3+} , and V^{3+} were observed after excitation with ultraviolet light, and, in the case of Ni^{3+} , after excitation with blue light. The magnetic properties are those to be expected for a $3d^7$ (Fe^+ and Ni^{3+}) and a $3d^2$ (V^{3+}) configuration in tetrahedral coordination. The quantitative features of the spectra reflect the systematic variations produced by covalency.

I. INTRODUCTION

IRON transition group impurities in II-VI compounds can participate in the photosensitive charge transfer processes important in luminescence and photoconductivity. The first observation of this phenomenon by electron paramagnetic resonance (EPR) was the conversion of Fe^{2+} to Fe^{3+} in CdS by visible light.¹ Subsequent EPR studies have shown that Fe^{3+} and Cr^+ in^{2,3} ZnS, and Fe^{3+} in⁴ ZnO are photosensitive. The charge states observed by EPR are generally produced or enhanced by the trapping of free electrons or holes created during illumination of the crystal with light of energy near to that of the band gap, and diminished with light of energy less than that of the band gap. However, we have produced Ni^{3+} EPR signals with light of energy less than that of the band gap.

This paper reports the results of an EPR study for isolated substitutional impurities having either a $3d^2$ or a $3d^7$ electronic configuration. These configurations are orbital singlets in a tetrahedral cubic field. The ions studied are Fe^+ ($3d^7$), Ni^{3+} ($3d^7$), and V^{3+} ($3d^2$) in cubic ZnS, and Ni^{3+} ($3d^7$) in ZnO. The paramagnetic resonance of Fe^+ has not previously been reported in tetrahedral coordination and that of Ni^{3+} has been observed only in GaAs.⁵ Their EPR spectra in cubic ZnS are similar to that of Co^{2+} reported by Ham *et al.*⁶ The EPR spectrum of Ni^{3+} in ZnO has the characteristic anisotropy of an $S=\frac{3}{2}$ system in a strong axial crystalline field.^{7,8} The V^{3+} EPR spectrum shows double-quantum

transitions analogous to those observed for Ni^{2+} and Co^{3+} in MgO .⁹

The quantitative variation in the EPR parameters reflects systematically the changing degree of covalency. Similar comparisons have been made by other workers.^{10,11}

II. EXPERIMENTAL PROCEDURE

Cubic ZnS crystals were doped with nickel and vanadium by vacuum deposition of a thin metal film and subsequent diffusion. The nickel diffusion was carried out in a sulfur atmosphere at 800°C for a few hours. The vanadium diffusion was carried out in a sulfur atmosphere at 1200°C for several days; the crystals were then annealed at 800°C to enhance the formation of the cubic zinc-blende modification. The ZnO crystals were prepared in a similar manner by diffusion in air at 1200°C. Iron was already present as an impurity in all of the ZnS crystals investigated by us.

The EPR measurements were made at 1.3°K with a 9-Gc/sec superheterodyne spectrometer with the klystron locked to the sample cavity. The samples were mounted on the end of a quartz light pipe which extended from the center of the TE_{011} cylindrical microwave cavity to the top of the low-temperature Dewar assembly. Illumination was provided by a 1500-watt high-pressure mercury-arc lamp (GE B-H6) and a Hilger-Watts D223 quartz-prism monochromator. Direct current was used for the arc in order to prevent 60-cps noise due to modulated photocurrents. The EPR signals were displayed either directly as absorption lines on an oscilloscope for rapid orientation of the crystal in the magnetic field, or as derivatives of absorption lines on a recorder. The ZnS samples were usually mounted with the $(1\bar{1}0)$ cleavage plane against the end of the light pipe so that the $[1\bar{1}0]$ crystal axis was parallel to the microwave magnetic field and perpendicular to the static magnetic field. The ZnO samples were mounted with the c axis in the horizontal plane.

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⁶ F. S. Ham, G. W. Ludwig, G. D. Watkins, and H. H. Woodbury, Phys. Rev. Letters 5, 468 (1960).

⁷ T. L. Estle and M. de Wit, Bull. Am. Phys. Soc. 6, 445 (1961).

⁸ G. W. Ludwig and H. H. Woodbury, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, p. 223.

III. RESULTS

 A. Fe⁺ (3d⁷) in Cubic ZnS

An intense anisotropic stress-sensitive EPR line was observed at liquid helium temperatures after ultraviolet illumination in nearly all ZnS samples examined. The samples investigated were of widely different purity and conductivity. This line is attributed to Fe⁺ which results from the trapping of a photoelectron by Fe²⁺. The EPR spectrum of Fe³⁺ is generally observed simultaneously with the Fe⁺ spectrum. Although a search has been made, no spectrum which can be attributed to Fe²⁺ has been observed.

The spin Hamiltonian for a 3d⁷ ion in tetrahedral symmetry⁶ is

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + u\beta\{S_x^3H_x + S_y^3H_y + S_z^3H_z - \mathbf{S}\cdot\mathbf{H}[3S(S+1)-1]\}, \quad (1)$$

where the first term is the usual Zeeman interaction¹² and the second term is one that has been shown by Bleaney¹³ and Koster and Statz¹⁴ to be allowed by symmetry. The cubic axes of the crystal are denoted by x , y , and z , and the spin S is $\frac{3}{2}$. Neglecting terms of the order $(u/g)^2$, the $M = -\frac{1}{2}$ to $M = +\frac{1}{2}$ transition occurs at the magnetic field

$$H = (h\nu/g\beta)[1 + (9u/5g)p], \quad (2)$$

where

$$p = 1 - 5(l^2m^2 + m^2n^2 + n^2l^2). \quad (3)$$

The direction cosines of the magnetic field with respect to the cubic axes of the crystal are l , m , and n . The resulting angular dependence of the Fe⁺ line is shown in Fig. 1. The agreement with Eq. (2) is quite good; the values of g and u giving the best fit to the experimental data are

$$g = 2.2515 \pm 0.0005, \\ u = -0.00565 \pm 0.00005.$$

The $M = \pm\frac{1}{2}$ to $M = \pm\frac{3}{2}$ transitions were not observed, presumably being broadened beyond detection by crystalline strains. In cubic crystals containing stacking faults, two Fe⁺ lines are observed whose angular dependence reflects the rotational twinning of the crystal.¹⁵ The linewidth of the observed Fe⁺ line is very sensitive to strain, the narrowest linewidths obtained being approximately one gauss.

 B. Ni³⁺ (3d⁷) in Cubic ZnS

An isotropic EPR line is observed in nickel-doped cubic ZnS crystals following irradiation with ultraviolet light. We ascribe this line to Ni³⁺ which is produced

¹² For an introduction to EPR and an explanation of the derivation and meaning of the spin Hamiltonian see, for example, Ref. 8.

¹³ B. Bleaney, Proc. Roy. Soc. (London) **A73**, 939 (1959).

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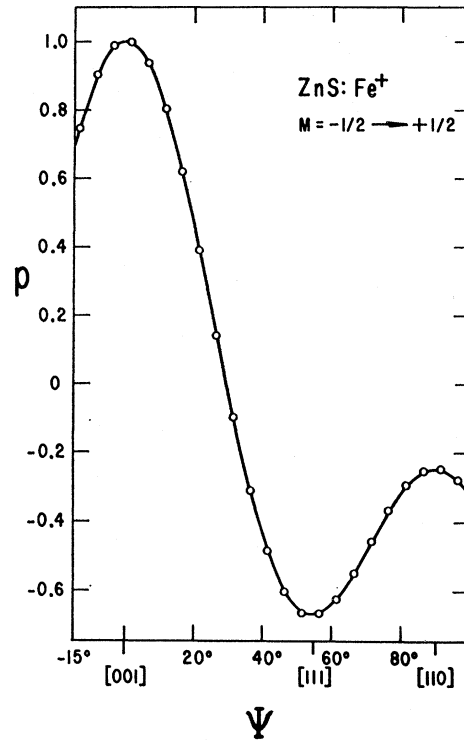


Fig. 1. Angular dependence of the Fe⁺ EPR line in cubic ZnS. The quantity p is defined by Eq. (3) and Ψ is the angle between \mathbf{H} and the [001] crystal axis. Rotation is about a [110] crystal axis. The solid curve is a plot of Eq. (3), and experimental points are shown by open circles. The crystal used was free of stacking faults and only the $M = -\frac{1}{2} \rightarrow +\frac{1}{2}$ transition was observed.

by photoholes trapped at Ni²⁺ impurities. Since Ni³⁺ is isoelectronic with Fe⁺ and Co²⁺, the spin Hamiltonian in Eq. (1) is applicable. The experimental values for g and u are

$$g = 2.1480 \pm 0.0005 \\ |u| \leq 0.0010.$$

The Ni³⁺ charge state can also be produced with blue light (3.1 eV) which is of insufficient energy for the production of electron hole pairs (band gap ≈ 3.6 eV). Weakliem,¹⁶ in his study of the optical absorption of Ni²⁺ ions in ZnS, observed a strong charge-transfer band at this same wavelength which we suggest is due to the direct excitation of a 3d electron into the conduction band. A similar behavior has so far not been observed for any of the other iron transition group ions.

 C. Ni³⁺ (3d⁷) in ZnO

Following irradiation with ultraviolet light, high-resistivity nickel-doped ZnO crystals show a highly anisotropic EPR signal which we ascribe to Ni³⁺. The intensity of the Ni³⁺ signal was compared at 1.3 and 4.2°K to the intensity of a Co²⁺ spectrum⁷ which occurred in the same sample. The intensities behaved in

¹⁶ H. A. Weakliem, J. Chem. Phys. **36**, 2117 (1962).

a similar fashion, suggesting that the zero-field splitting for Ni^{3+} is several cm^{-1} like that of Co^{2+} . Thus, it is assumed that $|2D| \gg h\nu$ and that $2D$ is positive. In this situation, only the $M = -\frac{1}{2}$ to $M = +\frac{1}{2}$ transition is observed. This transition is conveniently described in terms of an effective spin Hamiltonian,⁸

$$\mathcal{H} = \beta[g_{11}'S_z'H_x + g_{11}'(S_x'H_x + S_y'H_y)], \quad (4)$$

where the effective spin S' is $\frac{1}{2}$. The experimentally observed effective g' factors are

$$g_{11}' = 2.1426 \pm 0.0005, \\ g_{11}' = 4.3179 \pm 0.0010.$$

As in the case of nickel-doped ZnS, the Ni^{3+} resonance in ZnO can also be produced with light having an energy less than the band gap (band gap $\simeq 3.2$ eV). This transition is very prominent near 2.8 eV, where a strong charge-transfer band in the optical spectrum of Ni^{2+} in ZnO has been observed.¹⁶ This is analogous to the case of Ni^{2+} in ZnS discussed in Sec. III B.

D. V^{3+} ($3d^2$) in Cubic ZnS

Cubic ZnS crystals doped with vanadium show an isotropic EPR spectrum at 1.3°K consisting of eight 20-G-broad hyperfine lines. These are superimposed by eight 0.5-G-wide lines whose intensities depend upon the microwave power in a manner consistent with interpreting them as arising from double-quantum transitions. Although the resonance is present in the dark, it is enhanced by ultraviolet light and diminished by visible and infrared illumination. We attribute these to single- and double-quantum transitions for the $S=1$, $I=\frac{7}{2}$ ground state of V^{3+} in the tetrahedral crystalline field of ZnS. The double-quantum transitions have been analyzed by means of the expression

$$g\beta H = h\nu - Am - (A^2/2h\nu)[(63/4) - m^2] \\ + O(A^4/h^3\nu^3), \quad (5)$$

which results from a perturbation treatment of a spin Hamiltonian containing the Zeeman and hyperfine interaction terms. As shown by Eq. (5), no third-order terms are present. The best fit to the experimental data is obtained for

$$g = 1.9433 \pm 0.0005, \\ |A| = (63.0 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}.$$

IV. DISCUSSION

A. The $3d^7$ Ions

Fe^+ , Co^{2+} , and Ni^{3+} are isoelectronic, each having seven $3d$ electrons. The 4F ground term of the free ion is split by a tetrahedral cubic crystalline field into two orbital triplets, 4T_2 and 4T_1 , and a ground-state orbital singlet, 4A_2 . Because of the relatively small splitting

between 4A_2 and 4T_2 and the large spin-orbit matrix element connecting them, the g factor is shifted appreciably from the free-electron g factor g_0 . This g shift, $\Delta g \equiv g - g_0$, is given approximately by $\Delta g = -8\lambda_e/10Dq$, where λ_e is the effective spin-orbit coupling constant and $10Dq$ is the energy splitting between 4A_2 and 4T_2 .

A comparison of the g factors observed for Co^{2+} in II-VI compounds^{6,7,17} with the results of the present investigations shows that the g shift for Ni^{3+} is roughly half that for Co^{2+} and Fe^+ . This can be understood qualitatively by considering the effects of the charge of the ion.¹⁸ The greater the charge, the closer the ligands will be pulled by the electrostatic force; thus, a stronger crystalline field and a larger value of $10Dq$ will result. A greater charge also results in a larger free-ion spin-orbit coupling constant, λ_0 ; however, λ_e/λ_0 will presumably be smaller for the greater charge because of the greater delocalization resulting from greater overlap with the closer ligands. The increase in $10Dq$ and the decrease in λ_e/λ_0 with increasing charge both tend to reduce Δg for greater charge. The increase in λ_0 is in the opposite direction. The values of λ_0 are approximately -115 cm^{-1} , -172 cm^{-1} , and -238 cm^{-1} for Fe^+ , Co^{2+} , and Ni^{3+} , respectively.¹⁹ The relative g shifts of Ni^{3+} and Co^{2+} are quite reasonable upon considering the above factors. However, Fe^+ does not show the same behavior and seems somewhat anomalous. More examples are required before further speculation is in order.

The second term in Eq. (1) was predicted by Bleaney¹⁸ and Koster and Statz¹⁴ and shown by Ham *et al.*⁶ to be important for Co^{2+} in tetrahedral symmetry. Ham *et al.*⁶ have derived the relationship $u = -25(g-2)^2/192$ between u and the g shift. Although this expression is unable to explain quantitatively either our results for Fe^+ or their results for Co^{2+} , it is consistent with the lack of observed anisotropy for Ni^{3+} in cubic ZnS. Similarly, no anisotropy has been observed for Ni^{3+} in GaAs.⁵

In ZnO one has a trigonal field in addition to the tetrahedral field considered above. The 4A_2 ground state is split into two Kramers doublets by the combined action of the trigonal field and the spin-orbit interaction. The two doublets can be described by a spin Hamiltonian of the form

$$\mathcal{H} = g_{11}\beta H_x S_x + g_{11}\beta(H_x S_x + H_y S_y) \\ + D[S_z^2 - \frac{1}{3}S(S+1)], \quad (6)$$

with $S = \frac{3}{2}$. The effective spin Hamiltonian of Eq. (4) describing the $M = \pm\frac{1}{2}$ levels can be obtained from Eq. (6) if $2D$ is much larger than $h\nu$. The effective g' factors

¹⁷ H. H. Woodbury and G. W. Ludwig, Bull. Am. Phys. Soc. 6, 118 (1961).

¹⁸ S. Geschwind and J. P. Remeika, J. Appl. Phys. 33, 370 (1960).

¹⁹ T. M. Dunn, Trans. Faraday Soc. 57, 1441 (1961).

of Eq. (4) are given by²⁰

$$\begin{aligned} g_{11}' &= g_{11}, \\ g_{1'} &= 2g_{11}\left[1 - \frac{3}{16}(\hbar\nu/2D)^2\right]. \end{aligned} \quad (7)$$

The fact that $g_{1'}$ is approximately twice g_{11} results because the off-diagonal matrix elements of the $M = \pm \frac{1}{2}$ matrix are twice as large for $S = \frac{3}{2}$ as for $S = \frac{1}{2}$. Dividing $g_{1'}$ by two gives a rough approximation to g_{11} which is very close to g_{11} . Both the parallel and perpendicular g shifts are very close to that observed for Ni^{3+} in cubic ZnS.

Arguments analogous to those used for Co^{2+} in tetrahedral symmetry suggest that additional terms cubic in spin operators and linear in the magnetic field should appear in the $S = \frac{3}{2}$ spin Hamiltonian of Eq. (6). However, these terms should be small, presumably of the order of the u term in cubic crystals, and will therefore only weakly couple the two Kramers doublets. They will therefore produce small additional terms in the expression for the g' factors but will not modify the angular dependence predicted by the spin Hamiltonian of Eq. (4).

The zero-field splitting $2D$ is positive and large for all $3d^7$ ions studied in the wurtzite lattice. The combined effects of the trigonal field and the spin-orbit interaction on the 4T_2 and 4A_2 levels yield the expression $2D = \lambda_e(g_{11} - g_{1'})$. Using the approximate anisotropy for Ni^{3+} in ZnO and the free-ion λ , a value for $2D$ of $+4 \text{ cm}^{-1}$ results. This is comparable to the one reported for Co^{2+} in ZnO.⁷

B. The V^{3+} Ion

The $3d^2$ configuration of V^{3+} behaves similarly to the $3d^7$ configuration in a tetrahedral cubic crystalline field. The threefold spin degeneracy of the ground-state orbital singlet is not split by the cubic field. However, predominantly axial strains will split the $M = \pm 1$ levels away from the $M = 0$ level. Hence the transitions from $M = \pm 1$ to $M = 0$ are broadened by strains while the direct transition from $M = -1$ to $M = +1$ is still rather sharp. This latter transition was observed at high microwave power levels by the simultaneous absorption of two quanta. Such double-quantum transitions have also been observed by other investigators; the analogous system, $3d^8$ in octahedral symmetry, has been studied by Orton *et al.*⁹ They have conclusively demonstrated this double-quantum character.

In addition to ZnS, V^{3+} has also been observed in CdS and ZnTe.¹⁷ The magnitude of the g shift increases with increasing atomic number of the group II or VI elements. Thus, the magnitude of the g shift for ZnS is least and for ZnTe is greatest. Presumably $10Dq$ is decreasing more rapidly than λ_e as the covalency and lattice parameter increase. The hyperfine interaction is

²⁰ More general expressions are given in Ref. 8. Equation (7.6) of Ref. 8 has an incorrect sign.

approximately the same for the sulfides and about 10% smaller for ZnTe. This behavior is analogous to that found for Mn^{2+} and results from the greater covalency of the telluride.¹¹

C. Photosensitivity of Iron Group Impurities

The photosensitivity of iron group impurities in II-VI compounds is well known. Copper and manganese are used extensively as activators, while iron, cobalt, and nickel are considered to be "killers."²¹ Avinor and Meijer²² have shown that vanadium acts as an activator, producing infrared luminescence in ZnS and CdS. The vanadium-activated luminescence and the similar behavior of cobalt²³ were explained by Allen²⁴ in terms of transitions between energy levels of the respective ions. EPR measurements have shown that chromium can be converted from the divalent state to the monovalent state³ and iron from the divalent state to the trivalent state^{1,2,4} by light.

In the present work it is shown that isolated iron, nickel, and vanadium impurities convert from the divalent state to others by the trapping of photoproduced carriers. Fe^{2+} was shown to be both a hole and an electron trap, while Ni^{2+} and V^{2+} were shown to be hole traps. However, Ni^{3+} can also be formed by the direct excitation of an electron from Ni^{2+} into the conduction band. The equality of the energy required for direct excitation and that of the charge-transfer band observed in the optical-absorption spectra of nickel-doped ZnS and ZnO suggest that the latter results from the direct ionization of Ni^{2+} .

The fact that many charge states of the ions in question have not been observed prevents us from making more complete statements about their optical properties. Our failure to observe Fe^{+} in ZnO and CdS and Ni^{3+} in CdS may be significant. This may indicate that these levels lie outside the forbidden energy gap and, therefore, are not populated in steady state. The failure to observe Ni^{3+} in CdS may be correlated with the lack of a resolved charge-transfer band in the optical-absorption spectrum of Ni^{2+} in CdS.²⁵

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²⁵ R. Pappalardo and R. Dietz, Phys. Rev. **123**, 1188 (1961).