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Covalency and the Paramagnetic Resonance of Mn^{++} in CdSe

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The paramagnetic resonance spectrum of divalent manganese has been measured in a single crystal of CdSe ($C_{6v}{}^4$) at 77°K. The parameters are $g=2.003\pm0.001$, $A=(-62.7\pm0.5)\times10^{-4}$ cm^{-1}, $D=(15.2\pm0.5)\times10^{-4}$ cm^{-1}, $\mathfrak{a}=(+14.3\pm1.0)\times10^{-4}$ cm^{-1}, $F=(-2.0\pm1.0)\times10^{-4}$ cm^{-1}. It is to be noted that in this hexagonal crystal the effect of the cubic field parameter $\mathfrak{a}$ is comparable to that of the axial field parameter D. The large value of $\mathfrak{a}$ is attributed to covalency effects. A comparison of the measured $\mathfrak{a}$ value with $\mathfrak{a}$ values found for Mn^{++} in other wurtzite and zincblende crystals shows that there is a correlation between the magnitude of the $\mathfrak{a}$ value and the amount of covalency. A similar correlation between the value of D and the amount of covalency is also found and accounts for the low value of D in CdSe.

INTRODUCTION

DIVALENT manganese has a $3d^5$ electron configuration and a $^6S_{5/2}$ ground state. Such a spherically symmetric ground state cannot be directly affected by a crystalline electric field. It has, however, long been known that a field splitting of this state does occur. This splitting is assumed to be due to an admixture of higher lying levels into the ground state. Physical mechanisms that can account for such admixing involve high-order processes consisting of a combination of the effects of crystalline field, spin-orbit coupling, and spin-spin interaction. The problem has been theoretically considered by Watanabe,[1] and more recently by Gabriel, Johnston, and Powell.[2] The latter makes an estimate of the cubic field parameter $\mathfrak{a}$ for various values of the strengths of the crystalline field and of the spin-orbit coupling. For Mn^{++} in fourfold coordination, as found in zincblende and wurtzite structures, $\mathfrak{a}$ is expected to be about 0.3×10^{-4} cm^{-1}.[3] Measurements[3,4] on Mn^{++} in cubic CdTe give $\mathfrak{a}=27.0\times10^{-4}$ cm^{-1}. This is some two orders of magnitude greater than predicted and is attributed to the effects of covalency since the predicted value is based on an ionic model. In this paper the values of $\mathfrak{a}$ and the hexagonal field parameters D and F are measured for Mn^{++} in hexagonal CdSe. Rather surprisingly, the values of $\mathfrak{a}$ and D are found to be of about the same magnitude in this crystal. A comparison of the $\mathfrak{a}$ and D values with those measured for Mn^{++} in other wurtzite and zincblende type crystals shows that there is a correlation between the values of $\mathfrak{a}$ and D and the amount of covalency. The amount of covalency in CdSe is such as to result in approximate equality of $\mathfrak{a}$ and D.

EXPERIMENTAL PROCEDURE

The single crystal of CdSe was grown by Kucza. The method used was one of vapor transport in an evacuated quartz tube. To the charge of CdSe 18 parts per million by weight of MnSe were added (0.0025 $M\%$) and the tube placed in a thermal gradient. A large single crystal was produced at the cold end of the tube. Large single crystals were also found in the residue at the hot end.

The apparatus used was a Varian V-4500 spectromter with 100-kc/sec modulation. The orientation of the sample relative to the magnetic field was varied by rotating the liquid-nitrogen Dewar containing the sample. (The Dewar has a narrow section which passes through the cavity.)

Theory of the Spectrum

The spectrum may be analyzed in terms of a spin-Hamiltonian first proposed by Bleaney and Trenam.[5] In this Hamiltonian the hexagonal and cubic terms are separated. To do this, the cubic field term requires a different set of axes than the hexagonal terms

$$\begin{aligned}H=g\beta\mathbf{H}\cdot\mathbf{S}+\tfrac{1}{6}\mathfrak{a}[&S_\xi{}^4+S_\eta{}^4+S_\zeta\\&-\tfrac{1}{5}S(S+1)(3S^2+3S-1)]\\&+\mathrm{D}[S_Z{}^2-\tfrac{1}{3}S(S+1)]\\&+(F/180)[35S_Z{}^4-30S(S+1)S_Z{}^2\\&\qquad+25S_Z{}^2-6S(S+1)+3S^2(S+1)^2].\end{aligned}$$

The z axis is chosen to be the c axis of the crystal. The terms in D and F are the second- and fourth-order terms of the hexagonal field. The $\xi\eta\zeta$ axes for the cubic term are three mutually perpendicular axes chosen so that the [111] axis of this system coincides with the z axis of the hexagonal system. Mn^{++} that substitutes for Cd^{++} can occupy either of the two inequivalent sites Cd^{++} has in wurtzite symmetry. This results in two ways in which the $\xi\eta\zeta$ axes may be chosen. The two sets $\xi\eta\zeta,\xi'\eta'\zeta'$ are related to one another by a 60° rotation about the common [111] axis. The effect on the spectrum is to split the fine structure lines into two components. The two components coincide when the magnetic field is oriented parallel or perpendicular to the c axis and also when the field is in the plane of the prismatic faces (type $10\bar{1}0$ planes). In these directions only $(\mathfrak{a}-F)$ may be determined. The quantities $\mathfrak{a}$ and F may be separated by measurements made in a general direction.

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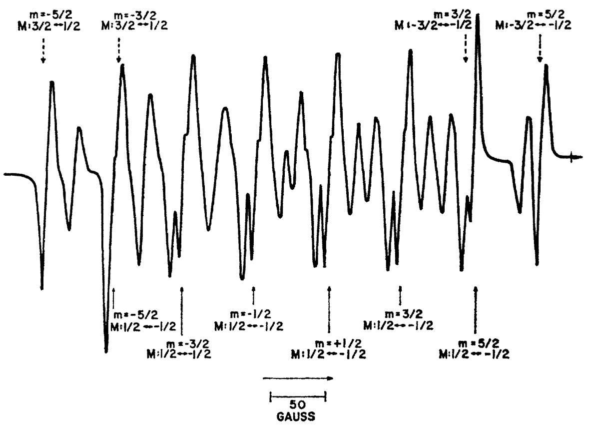

FIG. 1. The electron paramagnetic resonance spectrum of Mn^{++} in CdSe with $H \| c$ axis. The derivative of the absorption curve is shown.

EXPERIMENTAL RESULTS

The spectrum was first observed at room temperature. The lines were 12 G wide and the fine structure lines were incompletely resolved. On cooling the sample to 77°K the linewidth was reduced to 5 G and the fine structure was easily resolved.

The spectrum at 77°K for H parallel to the c axis is shown in Fig. 1. The $M=\frac{1}{2} \rightarrow M=-\frac{1}{2}$ transition of each hyperfine group is identified by the solid arrows. The sign of A has been assumed negative since A has been found to be negative for all Mn^{++} spectra so far measured. The sign of D may be found by examining the separations of the $M=\pm\frac{3}{2} \leftrightarrow M=\pm\frac{1}{2}$ transition at low and high fields. From Fig. 1, where these transitions are indicated dotted, the separation of this transition between the $m=-\frac{5}{2}$ and $m=-\frac{3}{2}$ hyperfine groups is less than between the $m=\frac{5}{2}$ and $m=\frac{3}{2}$ groups. This shows that D is of opposite sign to A, i.e., D is positive.[6] Detailed measurements on the spectrum of Fig. 1 yield the values

$$g=2.003\pm0.001,$$
$$A=-62.7\pm0.5\times10^{-4}\ \mathrm{cm}^{-1},$$
$$D=15.2\pm0.5\times10^{-4}\ \mathrm{cm}^{-1}$$
$$(a-F)=16.3\pm0.5\times10^{-4}\ \mathrm{cm}^{-1}.$$

The spectrum taken with the magnetic field oriented in the $(11\bar{2}0)$ plane in a direction 30° from the c axis is shown in Fig. 2. One notices that the $M=\pm\frac{5}{2} \leftrightarrow M=\pm\frac{3}{2}$ and the $M=\pm\frac{3}{2} \leftrightarrow M=\pm\frac{1}{2}$ have split into two. For the $m=-\frac{5}{2}$ and $m=+\frac{5}{2}$ hyperfine groups this splitting has been indicated in the figure. From an analysis of this spectrum as well as others taken for several orientations of the magnetic field in the $(11\bar{2}0)$ plane, the contributions of a and F could be separated. The values of a and F found were

$$a=(14.3\pm1.0)\times10^{-4}\ \mathrm{cm}^{-1},$$
$$F=(-2.0\pm1.0)\times10^{-4}\ \mathrm{cm}^{-1}.$$

DISCUSSION OF THE RESULTS

The values of g and A had been previously measured by Matamura[7] for CdSe powder at room temperature. The value found for g for a single crystal of CdSe at 77°K agrees with his. However, the value of A is somewhat higher, $(-62.7\pm0.5)\times10^{-4}$ cm^{-1} compared to his -61.5×10^{-4} cm^{-1}. The difference is probably due to the broader lines at room temperature. In addition, Matamura's measurements were made on powders which would have the effect of further broadening the lines due to the smeared out fine structure lines.

As previously indicated, the values of a and D were found to be approximately equal. The value of $a=14.3$ $\times10^{-4}$ cm^{-1} is some 50 times the value of 0.3×10^{-4} cm^{-1} (2,3) expected for Mn^{++} in zincblende and wurtzite symmetry. Some insight into the reason for this discrepancy is obtained by plotting the a values that have been measured for Mn^{++} in these symmetries against the amount of ionicity in the Mn^{++} anion bonds. The latter is determined from the empirical formula proposed by Pauling.[8] For the wurtzite compounds other than CdSe only the values of $(a-F)$ have been measured. For these compounds it was assumed $a \sim (a-F)$ and the measured values of $(a-F)$ are actually plotted. For example, in ZnS a has been measured for cubic ZnS and found equal to $(7.80\pm0.06)\times10^{-4}$ cm^{-1}.[9] For hexagonal ZnS the value of $(a-F)$ was measured to be $(7.6\pm1.0)\times10^{-4}$

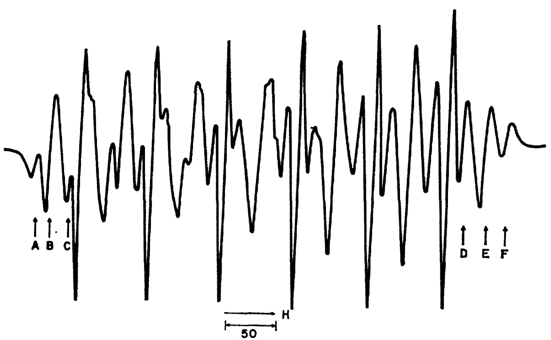

FIG. 2. The electron paramagnetic resonance spectrum of Mn^{++} in CdSe with H oriented in the $11\bar{2}0$ plane 30° from the c axis. (A) $m=-\frac{5}{2}$; $M: \frac{5}{2} \leftrightarrow \frac{3}{2}$, p. (B) $m=-\frac{5}{2}$; $M: \frac{5}{2} \rightarrow \frac{3}{2}$, p'; $M: \frac{3}{2} \rightarrow \frac{1}{2}$, p'. (C) $m=-\frac{5}{2}$; $M: \frac{3}{2} \leftrightarrow \frac{1}{2}$, p. (D) $m=\frac{5}{2}$; $M: -\frac{3}{2} \leftrightarrow -\frac{1}{2}$, p. (E) $m=\frac{5}{2}$; $M: -\frac{3}{2} \leftrightarrow \frac{1}{2}$, p'; $M: -\frac{5}{2} \leftrightarrow -\frac{3}{2}$, p'. (F) $m=\frac{5}{2}$; $M: -\frac{5}{2} \leftrightarrow -\frac{3}{2}$, p. The symbols p and p' refer to the two inequivalent sites.

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[6] For a review of determining the relative signs of A and D, the reader is referred to W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), pp. 71–75.

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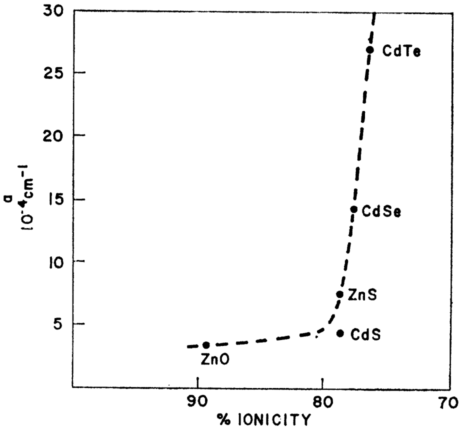

FIG. 3. A plot of the cubic field parameter α vs the ionicity of the Mn^{++} anion bonds.

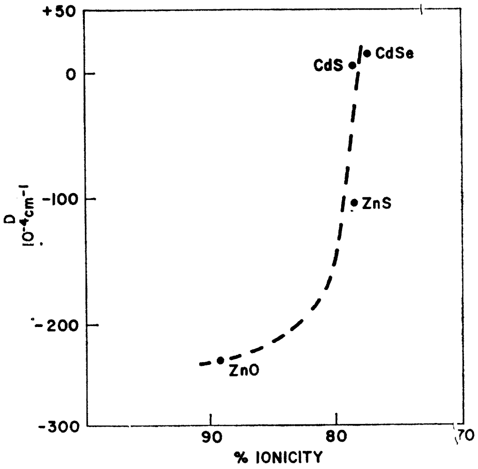

FIG. 4. A plot of the hexagonal field parameter D vs the ionicity of the Mn^{++} anion bonds.

cm^{-1}.[10] Figure 3 shows that the value of α increases markedly with increasing covalency. No significance is to be attached to the dashed curve which was drawn in to indicate the trend. No calculations of the effect of covalency on α have as yet been carried out.

A calculation of the effect on D of covalency and overlap of wave functions between the impurity and its neighbors was carried out by Kondo[11] for Mn^{++} ions in octahedral symmetry. Kondo showed that both the overlap of wave functions and covalency were important for Mn^{++} in alkali halides. The calculation has not been extended to fourfold coordination. That it is important for Mn^{++} in wurtzite symmetry may be inferred from Fig. 4 where D has been plotted against ionicity. The value of D is, of course, also dependent on the magnitude of the trigonal distortion in these compounds. However, x-ray determinations of the c/a ratios of these compounds show that they are equal to each other within 1% (~1.61). The variation of D as shown in Fig. 4 may, therefore, be ascribed to the effects of covalency.

It is, therefore, seen that the apparent paradox of the cubic field parameter of Mn^{++} being comparable to the hexagonal field parameter in hexagonal CdSe arises due to covalent effects.

A dependence of the value of the hyperfine structure parameter A on covalency had been previously pointed out by Matamura.[7] Covalency effects are, thus, significant for all the resonance parameters of Mn^{++} in zincblende and wurtzite symmetry.

ACKNOWLEDGMENTS

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