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Lattice-Site Distortions in Cobalt-Doped Cadmium Difluoride

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An investigation of the electron spin resonance spectrum of Co^{2+}–CdF_2 as a function of cobalt concentration and temperature indicates the existence of two inequivalent sites for the higher concentrations of cobalt.

Introduction

Recent investigations of the effect of substitution of transition metal ions into CdF_2 have brought to the fore some interesting observations pertaining to guest–host relationships. Measurement of the electronic spectrum of Co^{2+} in CdF_2[2] indicated the presence of a centrosymmetric cobalt site at low cobalt concentrations but an asymmetric site at high cobalt concentrations.

Similar measurements for Ni^{2+} and Cr^{3+} in CdF_2[3] strongly indicate the retention of a center of symmetry at the substitutional site within accessible dopant concentration ranges.

While a distortion mechanism was proposed to account for the observed behavior in the case of Ni^{2+} and Cr^{3+}, it was not possible to come to a suitable conclusion for Co^{2+}–CdF_2. In order to provide further insight into this problem we have investigated the electron spin resonance spectrum of Co^{2+} in CdF_2 as a function of both temperature and Co^{2+} concentration.

Experimental Section

Crystals of 0.5, 3.5, and 8 mol % of Co^{2+} doped in CdF_2 were grown by the Bridgeman technique using high-purity CdF_2 as described in ref 2.

The X-band electron paramagnetic resonance spectrometer, constructed in this laboratory,[4] was essentially of the standard bridge type using a circulator with the same cavity. A separate bucking loop was used which allowed signal detection at constant detector diode bias. The klystron was ac stabilized[5] using 1-kHz modulation of the reflector voltage. The resonance signal was amplified using standard phase-sensitive detection techniques with external magnetic field modulation of 10 kHz. In order to check modulation effects, the spectra were checked at all temperatures using 400 Hz.

The sample was placed in a TE 102 cavity of our design which allowed the crystal to be rotated. The cavity fit into the inside section of a four-walled glass cryogenic dewar for low-temperature measurements.

The magnetic field was calibrated during any given run using a Rawson–Lush Type 940 rotating-coil gaussmeter. A Hewlett-Packard 5245L frequency counter with a 5255A high-frequency plug-in was used to determine the oscillator frequency of the klystron.

Results

Electron paramagnetic resonance spectra were recorded for crystals containing 0.5 and 3.5 mol % at both 77 and 4.2°K and for the 8 mol % at 77°K. Lines in none of these crystals could be seen at room temperature. Representative lines are shown in Figures 1 and 2. The data are summarized in Tables I and II showing the results at 77 and 4°K, respectively. Two lines were observed, one at "$g = 2$" and a generally broader line in the region of "$g = 4$." The resonance lines were all partially asymmetric and showed a structure which changed slightly upon crystal rotation and markedly for different concentration. A significant anisotropy was not observed. No hyperfine structure was observed for these concentrations as reported by Hall and Hayes[6] for crystals of CdF_2 containing less than 0.05% Co^{2+}. The g values for the high-field lines represent an average value taken between the two peaks of the derivative of absorption. Since the lines, especially at liquid N_2 temperature, are not narrow or symmetrical, the g values listed do carry uncertainty. Even more question exists for the assignment of an "average g" value for the low-field lines where the derivative of absorption signal is not clear. The basic features of these lines, however, are valuable and a reasonable interpretation can be advanced as shown in the following section. A signal due to Mn^{2+} impurity which could not be removed is seen superimposed on the Co^{2+} signal. These results will be reported elsewhere.[7]

TABLE I[a]

% Co^{2+}	Resonance line	ΔH (peak to peak), G	g_{eff}
0.5	I	1140	3.79 ± 0.005
	II	687	2.17 ± 0.005
3.5	I	590	4.75 ± 0.005
	II	500	2.42 ± 0.005
8.0	I	720	4.66 ± 0.005
	II	850	2.10 ± 0.005

[a] At 77°K.

TABLE II[a]

% Co^{2+}	Resonance line	ΔH (peak to peak), G	g_{eff}	"8λ"/$10Dq$
0.5	I	550	4.56 ± 0.005	0.306 ± 0.005
	II	190	2.306 ± 0.005	
3.5	I	910	4.26 ± 0.005	0.445 ± 0.0005
	II	300	2.445 ± 0.005	

[a] At 4.2°K.

Discussion

It will be convenient to discuss these epr data in two sections, namely, the higher field line near "$g = 2$" and the lower line in the region of "$g = 4$."

(a) **High-Field Line.**—The high-field line can be explained if one assumes the Co^{2+} is sitting substitutionally in a Cd^{2+} cubic site. The structure of CdF_2 calls for a Cd^{2+} site at the center of a cube of eight F^- ions. For Co^{2+}, a d^7 ion, the orbital angular momentum

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[1] (a) Abstracted in part from the thesis submitted to the Physics Department, University of Wyoming, 1971. (b) Department of Chemistry. (c) Department of Physics.

[2] C. Simo, E. Banks, and S. L. Holt, *Inorg. Chem.*, **9**, 1446 (1969).

[3] C. Simo and S. L. Holt, *J. Inorg. Nucl. Chem.*, **32**, 457 (1970).

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[5] C. P. Poole, "Electron Spin Resonance," Interscience, New York, N. Y., 1967.

[6] T. P. P. Hall and W. Hayes, *J. Chem. Phys.*, **32**, 1871 (1960).

[7] B. Oral, S. L. Holt, and A. B. Denison, submitted for publication in *J. Inorg. Nucl. Chem.*

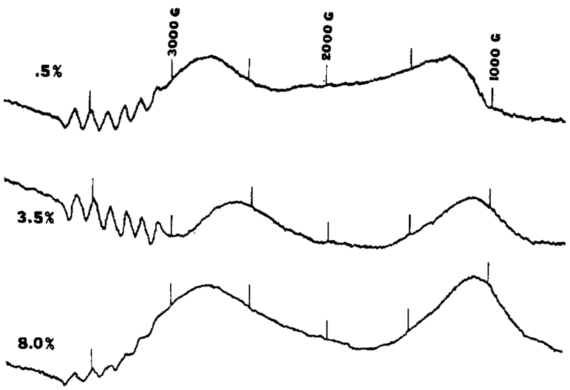

Figure 1.—Electron paramagnetic resonance spectra of Co^{2+} in CdF_2 at 77°K. Field markers are in gauss.

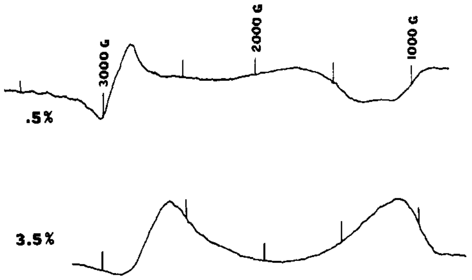

Figure 2.—Electron paramagnetic resonance spectra of Co^{2+} in CdF_2 at 4.2°K. Field markers in gauss.

state is ^4F. In the tetrahedral or cubic environment the ^4F state splits into an orbital singlet ground state ($^4A_{2g}$) and higher lying orbital triplets $^4T_{2g}$ and $^4T_{1g}$. The proximity of the $^4A_{2g}$ state to the $^4T_{2g}$ state causes rapid spin-lattice relaxation between the electronic spin levels so that the paramagnetic resonance is only observed at low temperatures. The center of the resonance line is shifted from that of a free electron due to spin–orbit induced mixing of $^4T_{2g}$ into $^4A_{2g}$ and is given by the expression

$$h\nu = g_{\text{eff}}\beta H \qquad (1)$$

where

$$g_{\text{eff}} = 2.0023 - \frac{8\lambda}{10Dq} \quad \text{(see ref 8, 9)} \qquad (2)$$

In all cases we have measured, the high-field line occurs at a g value higher than that for the free electron. This is consistent with eq 2, assuming that λ is negative for the d^7 ion. The lines measured at liquid nitrogen temperature are distorted enough to make the actual determination of $8\lambda/10Dq$ unreliable. Using eq 2 and the average g_{eff} given in Table I the values of $8\lambda/10Dq$ are calculated to range from 0.10 to 0.42. This range of spin–orbit coupling is too large to be reasonable and must indicate the presence of additional site distortions about the cubic site. For the resonances at liquid He the high-field lines appear more symmetric and for the 0.5% Co^{2+} case also narrower. The value of 0.306 ± 0.005 found for the spin–orbit term at liquid He for the 0.5% doping is larger than the value of 0.276 ± 0.005 reported by Hall and Hayes for their 0.05% crystal.[6] We would find a value of λ equal to -145 cm^{-1} consistent with a measured $10Dq$ of 3800 cm^{-1} by Banks, *et al.*[2]

(b) **Low-Field Line.**—As mentioned, the resolution of the low-field lines and the determination of their g values is not as clear as that for the higher field lines. These lines are broader and less symmetric. There is even indication of structure on one of these resonances (see Figure 1). On the other hand, these resonances do remain in the region of $g = 4$ and do not change their position to magnetic field higher than that for the "$g = 2$" lines. This fact appears to rule out the most expected mechanism, namely, the presence of significant zero-field splitting, which would arise from a noncentrosymmetric site. The $S = {}^3/_2$ spin system might be expected to show zero-field splitting in a nonspherical site with the resulting nonzero D and E described by the spin Hamiltonian

$$\mathcal{H} = g\beta\vec{S}\cdot\vec{H} + D[S_z^2 - {}^1/_3S(S+1)] + E(S_x^2 - S_y^2) \qquad (3)$$

Even for axial symmetry ($E = 0$) and $D \ll g\beta H$, the ${}^3/_2 \longleftrightarrow +{}^1/_2$ transition would show a minimum anisotropy of resonance given by

$$h\nu = g\beta H + D[3\cos^2\theta - 1] \qquad (4)$$

This expression states that for some orientations the line observed at low fields ("$g = 4$") must also move to higher fields above $g = 2$. This shift has not been observed for any of the crystals at any orientation. Another possibility was considered, namely, the spectra observed were a sum of sites each having an axial or rhombic distortion. The result of summing would not show a center of gravity at "$g = 4$" with no contribution at fields higher than the $g = 2$ resonance.

A possible explanation is that the eightfold cubic site has become distorted toward an octahedral configuration. This could occur if two of the neighboring fluorines on opposite corners of the cube moved out and the six remaining fluorines adjusted to approximate an octahedron. Such a distortion has been postulated in CdF_2 for ions of Ni^{2+} and Cr^{3+}.[2] In a perfect octahedral site g is predicted to be 4.3372. The Co^{2+} ion resonances measured in our CdF_2 host are near this predicted value.

The theory of the Co^{2+} ion in an octahedral site shows the three nondegenerate orbital levels of the ^4F state are inverted from the pure cubic or tetrahedral case. The orbital scheme becomes a $^4T_{1g}$ ground level followed at $({}^4/_5)10Dq$ by $^4T_{2g}$ and then at $10Dq$ above $^4T_{2g}$ by the singlet $^4A_{2g}$. Following the description used by Low[10] based on an earlier work by Abragam and Pryce,[11] we can derive the effective g splitting of the lowest triplet level. This lowest orbital triplet is fourfold spin degenerate. The overall 12-fold degeneracy is partially removed once again by spin–orbit coupling. One may choose a fictitious net orbital angular momentum $l' = 1$ for the $^4T_{1g}$ state and then define a net angular momentum $m = l_z' + S_z$. For an isotropic spin–orbit interaction we can consider the spin–orbit interaction as

$$H_{\text{so}} = \alpha\lambda[L_xS_x + L_yS_y + L_zS_z] \qquad (5)$$

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[8] B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1966, Chapter 10.

[9] B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1966).

[10] W. Low, *Phys. Rev.*, **109**, 256 (1958).

[11] A. Abragam and H. M. L. Pryce, *Proc. Roy. Soc., Ser. A*, **205**, 135 (1951).

where α is determined by the amount of admixture of the P state in the ^{4}F state. In our discussion we will consider the admixture to be zero which forces α to be $^3/_2$. To obtain the energy levels of the ^{4}F state when split by spin–orbit interaction, one uses a representation in which l_z' and S_z are diagonal. Solving the characteristic matrices in this representation one finds the splitting of the $^4T_{1g}$ to be $^{15}/_4\lambda$ for $m = \pm{}^1/_2$; $^6/_4\lambda$ for $m = \pm{}^1/_2, \pm{}^3/_2$; and $-{}^9/_4\lambda$ for $m = \pm{}^1/_2, \pm{}^3/_2, \pm{}^5/_2$. The lowest sublevel is $^{15}/_4\lambda$, since λ is negative for the d^7 ion. This level will be split by a magnetic field into $|m = {}^1/_2\rangle$ and $|m = -{}^1/_2\rangle$. The wave functions are given as

$$|{}^1/_2\rangle = \frac{1}{\sqrt{2}}|-1, {}^3/_2\rangle - \frac{1}{\sqrt{3}}|0, {}^1/_2\rangle + \frac{1}{\sqrt{6}}|1, -{}^1/_2\rangle \quad (6)$$

$$|{}^1/_2\rangle = \frac{1}{\sqrt{2}}|1, -{}^3/_2\rangle - \frac{1}{\sqrt{3}}|0, -{}^1/_2\rangle + \frac{1}{\sqrt{6}}|-1, {}^1/_2\rangle \quad (7)$$

For a pure octahedral field the magnetic splitting is described by an isotropic $g = g_{||} = g_\perp$ and $h\nu = g\beta\vec{H}\cdot\vec{S}$ with

$$g = 2\langle{}^1/_2|L_z + 2S_z|{}^1/_2\rangle \text{ or } g = 4.333 \quad (8)$$

Low[10] has pointed out that to second order the spin–orbit interaction can result in mixing some of the $^4T_{2g}$ into the $^4T_{1g}$ state with the additional contribution to g of $-({}^{15}/_2)(\lambda/10Dq)$. In addition, in our case we expect if the site has been distorted toward the octahedral symmetry, the sites in general will not be pure. Distortions on octahedral symmetry will produce a slight anisotropic effect which we do observe in our broad lines.

We must now consider the earlier optical measurements on Co^{2+}–CdF_2. The important results of these experiments are: (1) The electronic spectrum of Co^{2+}–CdF_2 does not appear to change in band shape or complexity with increasing Co^{2+} concentration but does from the outset show a rather complex series of maxima. (2) The optical intensity-giving mechanism appears to be vibronic at low Co^{2+} concentrations but is essentially static at high Co^{2+} concentrations; *i.e.*, there are no Co^{2+} sites which retain a perfect center of symmetry.

These results are, in the main, consistent with our esr results. It appears that there is but one Co^{2+} site at very low Co^{2+} concentrations[6] and that this site is a cubic eightfold coordinated one. As the concentration of Co^{2+} is increased, the lattice begins to distort. One type of distortion involves the slight elongation of two CoF bonds and produces the pseudooctahedral resonance at $g = 4$. The second type of distortion most likely produces a site which has four nearest fluorides in a tetrahedral arrangement (this is the $g = 2$ site). By the time a concentration of 8 mol % Co^{2+} has been reached all Co^{2+} ions are in one of these two types of sites.

It is clear that the number of Co^{2+} ions in pseudooctahedral sites increases from zero to a concentration approximately equal to that of the "tetrahedral" sites (the epr signal at $g = 4$ is of equal intensity to that at $g = 2$ for a Co^{2+} concentration of 8%). It is also evident that the $g = 2$ sites are no longer cubic at 8% Co^{2+} as there is no vibronic contribution to the intensity at this concentration.

On the other hand, the symmetry of both the "$g = 2$" and "$g = 4$" sites must be similar to one another and to the original eightfold cubic site as only minor changes appear in the optical spectrum as the concentration of Co^{2+} is increased.

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The Difluorochlorate(V) Anion, $ClO_2F_2^-$. Vibrational Spectrum and Force Constants

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The infrared and the Raman spectra of solid $CsF \cdot ClO_2F$ have been recorded. They are consistent with a $ClO_2F_2^-$ anion of symmetry C_{2v}. The structure can be derived from a trigonal bipyramid, where the two F atoms occupy the axial and the two O atoms and the lone electron pair occupy the equatorial positions. A modified valence force field has been computed for $ClO_2F_2^-$, indicating double-bond character for the ClO bonds and rather weak ClF bonds with high ionic contributions.

Introduction

Huggins and Fox have recently reported[1] the existence of $CsClO_2F_2$. However, they did not succeed in obtaining any spectroscopic or structural data on this interesting compound. In this paper, we report the vibrational spectrum and the results of a force-field computation for $CsClO_2F_2$.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 IF4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ±0.1%). Chloryl fluoride (prepared in this laboratory from $KClO_3$ and F_2[2]) was purified by fractional condensation. Its purity was determined by measuring its vapor pressure and infrared spectrum. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. Because of their hygroscopicity, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin–Elmer Model 337 and 457 spectrophotometers in the range 4000–250 cm^{-1}.

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(2) A. Engelbrecht, *Angew. Chem.*, **66**, 442 (1954).