

## Jahn-Teller Splittings in the Optical Absorption Spectra of Divalent Iron in Cadmium-Chloride-Type Crystals\*†

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Measurements of the Jahn-Teller splittings of the  ${}^5T_{2g}({}^6D) \rightarrow {}^5E_g({}^6D)$  optical transition of divalent iron in the near infrared are reported for  $\text{CdCl}_2$ ,  $\text{CdBr}_2$ ,  $\text{MgCl}_2$ , and  $\text{MnCl}_2$  crystals containing about 15% divalent iron and for ferrous chloride. The variation of the magnitude of the observed splittings with temperature for the various host crystals is discussed and compared with theoretical predictions.

### I. INTRODUCTION

THE optical absorption spectra of many divalent iron compounds show the main spin-allowed transition  ${}^5T_{2g}({}^6D) \rightarrow {}^5E_g({}^6D)$  as a broad band split into two components separated by frequencies ranging from 500 to 4000  $\text{cm}^{-1}$ .<sup>1</sup> In cubic and trigonal symmetry compounds, the splittings are attributed to dynamic Jahn-Teller (JT) effects of the type discussed by Longuet-Higgins *et al.*,<sup>2</sup> O'Brien,<sup>3</sup> and Sturge.<sup>4</sup>

The purpose of the work to be described here is to supplement earlier work<sup>1</sup> on these splittings by a detailed investigation of the variation of the splittings with temperature and host crystal. Cadmium-chloride-type crystals were chosen for such studies because they possess the following advantages:

(a) The crystals have  $D_{3d}$  trigonal symmetry and the transition-metal ions are in sites not very distorted from cubic symmetry.

(b) The six isomorphous crystals cadmium chloride, cadmium bromide, magnesium chloride, ferrous chloride, manganese chloride, and zinc bromide are all suitable as hosts for the measurement of the main quintet-quintet transition of divalent iron. A comparison of the spectra for all six crystals yields the effect of variation in both cation and anion for a single-crystal structure.

The spectra of the five crystals cadmium chloride, cadmium bromide, magnesium chloride, ferrous chloride, and manganese chloride, all containing divalent iron, were measured over the 4–300°K temperature range and the splittings of the main absorption band near 7000  $\text{cm}^{-1}$  determined. Since the measurements are made on broad bands, there is a limit to the accuracy that can be achieved because of uncertainties in the location of the exact positions of band maxima; this

has to be taken into account in any analysis of the measurements. In this work, the temperature and lattice-frequency dependences of the band splittings were extracted from the experimental data and analyzed on a phenomenological basis.

### II. EXPERIMENTAL DETAILS AND RESULTS

The crystals were grown from the melt by the Stockbarger method. The hydrated chlorides and bromides were dehydrated over a period of days under vacuum, mixed together in the appropriate proportions, sealed in quartz ampoules, and lowered through a sharp temperature gradient. The resultant crystals were clear boules with cleavage planes usually at about 45° to the axis of the quartz tube. In general, they are moderately hygroscopic, and so were stored in a vacuum desiccator. The hygroscopic nature was found to vary markedly for the different crystals. Cadmium bromide is fairly resistant to atmospheric attack, while zinc bromide is strongly deliquescent and needs careful handling; the other crystals show intermediate behavior. For use, the crystals were cleaved just prior to mounting in an optical cryostat.

The nominal concentration of divalent iron chosen for initial doping was 15% and the crystals readily grow with this level of dopant. Investigations on manganese-, cobalt-, nickel-, and copper-doped crystals, all of which are strongly colored, show that the transition-metal ions are uniformly distributed through the crystals for thicknesses up to 5 mm. The actual concentration of divalent iron contained in each crystal was determined by comparison of the band intensities with that of ferrous chloride.

The optical absorption spectra of the five crystals were measured over the temperature range 4–300°K on a Cary 14R recording spectrophotometer. The sixth crystal, zinc bromide, could not be measured because the crystals grown were too small. The crystals were mounted in an Andonian variable-temperature Dewar in which the crystals are cooled by thermal contact with a copper block. Their temperature could be adjusted by balancing the heat input from an electrical heater against the cooling effect produced by exchange gas coupling of the liquid refrigerant to the copper

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<sup>1</sup> G. D. Jones, *Phys. Rev.* **155**, 259 (1967).

<sup>2</sup> H. C. Longuet-Higgins, U. Opik, M. H. L. Pryce, and R. A. Sack, *Proc. Roy. Soc. (London)* **A244**, 1 (1958).

<sup>3</sup> M. C. M. O'Brien, *Proc. Phys. Soc. (London)* **86**, 847 (1965).

<sup>4</sup> M. D. Sturge, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1967), Vol. 20, p. 91.

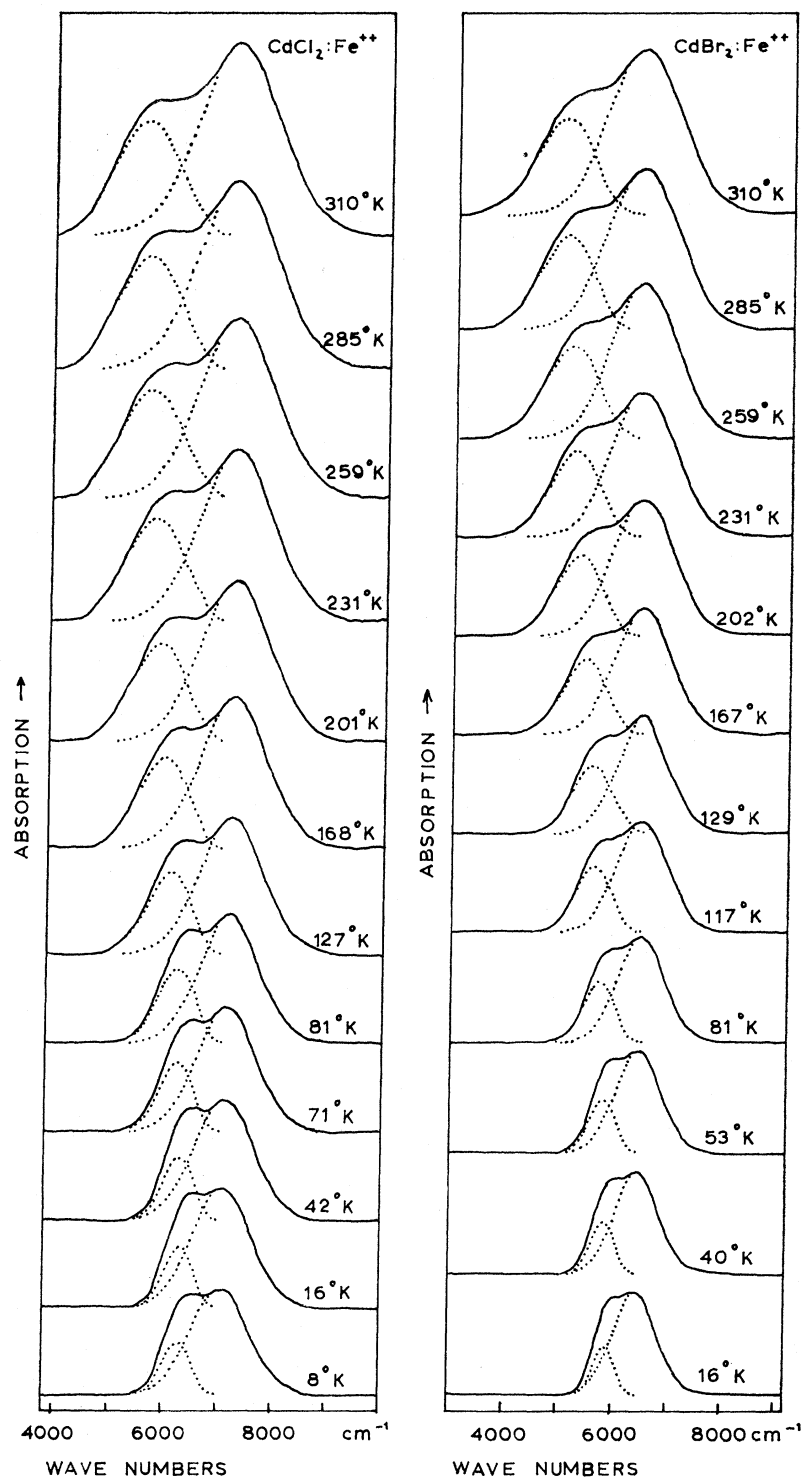


FIG. 1. Absorption-band contours of the  ${}^5T_{2g}({}^5D) \rightarrow {}^5E_g({}^5D)$  transition of divalent iron in cadmium chloride and cadmium bromide crystals for various temperatures.

block. The temperature of the crystals was monitored by a copper-constantan thermocouple.

The crystals cleave perpendicular to the  $c$  axis, and all the variable-temperature spectral runs were recorded with the direction of propagation of light parallel to the  $c$  axis. These spectra are thus axial. The

polarization of the bands for  $\text{CdCl}_2:\text{Fe}^{2+}$  was also investigated using HR-type Polaroid film and found to be negligible.

The absorption-band contours for the cadmium chloride and cadmium bromide crystals are shown in Fig. 1 for several temperatures. These have been

TABLE I. Splittings of the main quintet-quintet transition  ${}^5T_{2g}({}^6D) \rightarrow {}^5E_g({}^6D)$  of divalent iron in cadmium-chloride-type crystals.

Temperature (°K)	Band maxima of high-frequency component (cm <sup>-1</sup> )	Band maxima of low-frequency component (cm <sup>-1</sup> )	Separation (cm <sup>-1</sup> )
1. Cadmium chloride containing 14% divalent iron			
8	7050	6290	760
16	7040	6270	770
42	7060	6265	795
71	7085	6205	880
81	7110	6175	935
127	7110	6020	1090
168	7125	5900	1225
201	7135	5800	1335
231	7140	5700	1440
259	7120	5580	1540
285	7130	5525	1605
310	7140	5485	1655
2. Cadmium bromide crystals containing 13% divalent iron			
16	6430	5875	555
40	6445	5850	595
53	6465	5805	660
72	6480	5740	740
81	6485	5720	765
117	6500	5620	880
129	6510	5595	915
167	6495	5440	1055
202	6475	5320	1155
231	6465	5220	1245
259	6470	5165	1305
285	6430	5055	1375
310	6435	5010	1425
3. Magnesium chloride containing 25% divalent iron			
8	7360	6610	750
52	7360	6560	800
82	7400	6515	885
129	7395	6385	1010
168	7395	6240	1155
201	7395	6140	1255
232	7390	6070	1320
259	7390	6010	1380
285	7390	5955	1435
310	7400	5880	1520
4. Manganese chloride crystal containing 7% divalent iron			
13	7200	6440	760
52	7215	6390	825
83	7200	6285	915
132	7220	6130	1090
170	7205	6000	1205
202	7240	5900	1340
233	7215	5820	1395
260	7210	5710	1500
286	7195	5670	1525
310	7195	5575	1620
5. Ferrous chloride			
8	7370	6620	750
83	7470	6500	970
133	7470	6350	1120
168	7460	6190	1270
202	7440	6060	1380
232	7430	6010	1420
260	7430	5930	1500
286	7430	5870	1560
310	7430	5820	1610

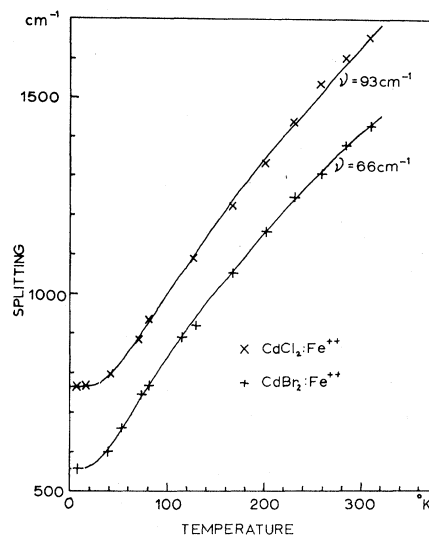


FIG. 2. Variation of the splitting of the  ${}^5T_{2g}({}^6D) \rightarrow {}^5E_g({}^6D)$  absorption band of divalent iron in cadmium chloride and cadmium bromide with temperature. The  $\nu$  values give the "effective" lattice frequency.

analyzed into two overlapping Gaussian components, also shown. The spectra of the remaining three crystals show similar behavior. The splittings of the bands are given by the separation of these Gaussian components and vary with temperature as shown in Fig. 2. Numerical values for the splittings at various temperatures are listed in Table I together with other spectral data. The splittings cannot be determined to better than 10% because of the uncertainties inherent in the analysis and the large breadth of the bands. Furthermore, the Cary spectrophotometer has some base-line oscillations in the near infrared due to the quartz optics used<sup>5</sup> and to atmospheric water absorption. These oscillations cause additional uncertainties on the 0.77-, 0.97-, 1.27-, 1.4-, 1.8-, and 2.2- $\mu$  regions and have to be corrected for. The data for cadmium bromide are the least affected by such corrections, since the band maxima lie outside these regions.

The oscillator strength of the absorption band was determined as  $10^{-5}$  for ferrous chloride. This value is typical of spin-allowed transitions of  $3d$  ions.<sup>6</sup>

### III. JAHN-TELLER SPLITTINGS

For divalent iron in a cubic crystal field, it has been shown<sup>3,7</sup> that the magnitude of the JT splitting is at least a factor of 10 greater for the upper  ${}^5E_g$  state than for the  ${}^5T_{2g}$  ground state and, to a good approximation, the  ${}^5T_{2g}$  state may be regarded as unsplit. The splitting  $\Delta\omega$  of the upper  ${}^5E_g$  level is given by Sturge,<sup>4</sup> for the

<sup>5</sup> M. E. Hills, A. L. Olsen, and L. W. Nichols, Appl. Opt. 7, 1437 (1968).

<sup>6</sup> C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill Book Co., New York, 1962).

<sup>7</sup> J. H. Van Vleck, Phil. Mag. 4, 269 (1960).

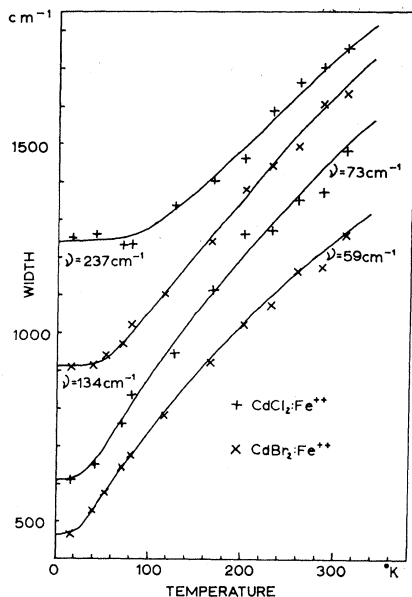


FIG. 3. Variation with temperature of the width of the two components of the  ${}^5T_{2g}({}^5D) \rightarrow {}^5E_g({}^5D)$  transition of divalent iron in cadmium chloride and cadmium bromide.

simple case of an octahedral complex having JT coupling to just one vibration mode  $\omega$ , as

$$\Delta\omega = 2(\delta E\hbar\omega)^{1/2} = (2\hbar A^2/m\omega)^{1/2},$$

where  $\delta E (= A^2/2m\omega^2)$  is the JT stabilization energy and  $A$  is a parameter representing the strength of the JT coupling.

O'Brien, in an earlier paper,<sup>3</sup> discusses the extension of the formula for the splitting to the case of a real crystal with continuous lattice modes and finds that

$$\Delta\omega = \left( \sum_i 2\hbar A_i^2/m_i\omega_i \right)^{1/2},$$

where  $A_i$  is the strength of the JT coupling to the  $i$ th mode,  $m_i$  and  $\omega_i$  refer to the  $i$ th mode, and the summation is over all modes of vibration contributing to  $e_g$  symmetry distortion at the ferrous ion site. Reasonable agreement is found between the splittings given by this formula and experimental data.<sup>3</sup>

The observed bands have a temperature-dependent splitting and the above formulas are for the zero-temperature splittings. The effect of temperature is obtained by multiplying the zero-temperature values by the factor  $[2n(\omega_i)+1]^{1/2}$ , where  $n(\omega_i)$  is the occupation number of the  $i$ th mode of vibration. It is one of the aims of the work reported here to correlate the observed temperature dependence of the splittings with this formula and so deduce the "effective" frequency of the vibration modes participating in the JT coupling.

The observed bands frequently show an asymmetric contour which varies with temperature. This has been

suggested<sup>3,4</sup> as evidence for the need to include the nuclear kinetic energy in the potential-energy calculation, as done by Slonczewski.<sup>8</sup>

#### IV. DISCUSSION OF RESULTS

In trigonal symmetry compounds, the only degenerate electronic levels are the doubly degenerate  $E$  levels and the JT interaction is that of an  $E$  electronic level with an  $e$  vibrational mode.<sup>9</sup> Both the  $E$  electronic level and the  $e$  vibrational mode are unsplit by a trigonal distortion from cubic symmetry, so that the lowering of symmetry from the cubic case introduces no new features in the analysis and the formula of Sec. III should be applicable. The following conclusions result:

(1) The formulas for the splittings imply that these should vary with the frequency of the lattice modes participating in the JT distortion. For the  $E_g$  electronic state investigated here, the relevant lattice modes are those of  $e_g$  symmetry about the ferrous ion site. These vibrations are almost identical for ferrous chloride and manganese chloride, since the crystal structures are the same and the ionic masses are almost equal. The JT splittings for iron in the two compounds should, therefore, be the same within experimental error, as shown in Table I.

(2) The JT splittings are similar in all the chlorides and are smaller in the one bromide measured by the square root of the ratio of chlorine to bromine mass.

(3) The splittings should increase with temperature according to the relation given by Sturge<sup>4</sup>:

$$\frac{\Delta\omega_{T^\circ\text{K}}}{\Delta\omega_{0^\circ\text{K}}} = \left( \frac{e^{\hbar\nu_i/kT} + 1}{e^{\hbar\nu_i/kT} - 1} \right)^{1/2}.$$

The data obtained for all five crystals were fitted to this formula with one "effective" lattice frequency  $\nu$  to represent the effect of the lattice phonon continuum of the crystal. Figure 2 shows the fit of the experimental data to curves of the appropriate  $\nu$  for cadmium chloride and bromide. For ferrous chloride, manganese chloride, and magnesium chloride the values of  $\nu$  are 89, 97, and 107  $\text{cm}^{-1}$ , respectively. A knowledge is required of the phonon dispersion curves for cadmium chloride to interpret the values of  $\nu$ . The  ${}^5T_{2g} \rightarrow {}^5E_g$  transition is parity-forbidden, and an odd-parity vibrational mode, different from those participating in the JT interaction, is required to make the transition observable and this mode can also contribute to the temperature dependence of the splitting. The values of  $\nu$  obtained in the analysis of the temperature dependences can thus only be regarded as semi empirical parameters, which reflect the over-all contribution of all the lattice vibrations to the band splitting.

<sup>8</sup> J. C. Slonczewski, Phys. Rev. **131**, 1596 (1963).

<sup>9</sup> P. J. Stephens, J. Chem. Phys. (to be published).

(4) The zero-temperature splitting is given by

$$\Delta\omega = (2hA^2/m\omega)^{1/2},$$

assuming one "effective" lattice frequency  $\nu$  ( $=\omega/2\pi$ ). The ratio of chloride to bromide splitting should be 1.27 using the values of  $\nu$  found for cadmium chloride and bromide from the temperature dependences. The observed ratio is 1.37.

(5) The bands vary in a characteristic manner with temperature. The lower-frequency component shifts markedly to lower energies with temperature, while the higher-frequency component remains almost constant. Such behavior was also observed in other compounds in previous work.<sup>1</sup> The behavior of the bands with temperature can be qualitatively understood on the basis of the configuration coordinate model.<sup>4</sup>

(6) The width of the two bands differs as shown in Fig. 3. The lower-frequency band is narrower. The temperature dependence can be fitted to expressions of the form<sup>10</sup>

$$\frac{\Delta\omega_T^\circ\text{K}}{\Delta\omega_0^\circ\text{K}} = \left( \coth \frac{h\nu}{2kT} \right)^{1/2},$$

yielding  $\nu=73$  and  $240\text{ cm}^{-1}$ , respectively, for the lower and upper bands of divalent iron in cadmium chloride and  $\nu=59$  and  $130\text{ cm}^{-1}$  for the two corresponding bands in cadmium bromide. These results are only approximate because of errors inherent in resolving the two bands from the over-all absorption curve. The difference in the linewidths of the two bands has been cited as evidence for the need to include the Slonczewski "pseudocentrifugal" term. However, it is predicted<sup>4</sup> that the higher-frequency band should be narrower and this is not the case.

(7) A measure of the intensity of the two bands is the product of the peak height with half-height width of the bands and this quantity is shown in Fig. 4 as a function of temperature.

<sup>10</sup> D. Curie, *Luminescence in Crystals* (Methuen and Co. Ltd., London, 1963), p. 51.

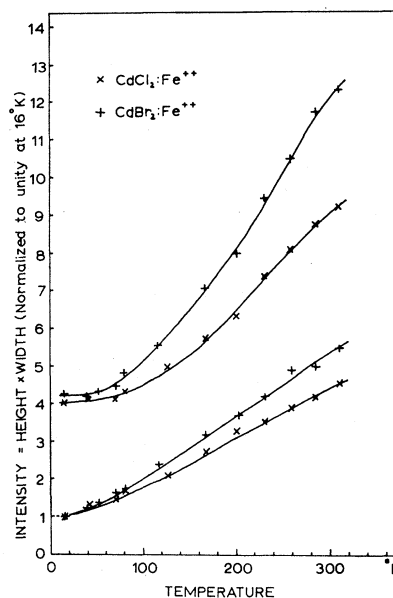


Fig. 4. Variation with temperature of the intensity of the two components of the  ${}^5T_{2g}({}^5D) \rightarrow {}^5E_g({}^5D)$  transition of divalent iron in cadmium chloride and cadmium bromide.

## V. CONCLUSIONS

Experimental data on the splittings of the near-infrared absorption band of divalent iron in cadmium-chloride-type crystals are sufficiently in agreement with theoretical formulas to substantiate the belief that the observed splittings are due to dynamic JT effects. The variation of the splittings with crystal lattice and with temperature can be interpreted in an approximate fashion by representing the lattice spectrum of the host crystals by a single effective frequency treated as a semiempirical parameter.

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