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Jahn-Teller Splittings in the Optical Absorption Spectra of Divalent Iron Compounds*

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Measurements of the Jahn-Teller splittings of the $^5T_{2g}(^5D) \rightarrow {}^5E_g(^5D)$ optical transition of divalent iron in the near infrared are reported for FeF_2, $KFeF_3$, $KMgF_3{:}Fe^{2+}$, $FeSiF_6{:}6H_2O$, $FeCl_2$, and $MgO{:}Fe^{2+}$. The effect of the site symmetry of the ferrous ion on the magnitude of the splittings observed is discussed.

INTRODUCTION

THE $3d^6$ energy level configuration applies to the optical absorption spectra of divalent iron compounds and this is characterized by one spin-allowed transition $^5T_{2g}(^5D) \rightarrow {}^5E_g(^5D)$ in the 10 000-cm^{-1} region and by several spin-forbidden quintet-triplet transitions at higher energies.

The optical absorption spectra of all the divalent iron compounds examined in this work show the spin-allowed quintet-quintet transition as a broad absorption band split into two components separated by frequencies ranging from 700 to 3600 cm^{-1}. This splitting corresponds to a lowering of the degeneracy of the upper ^5E_g states of the optical transition. A similar splitting may be present in the ground state, but such a splitting by itself would not give rise to the spectra observed as only the lowest component would be populated at low temperature.

The splitting cannot be due to spin-orbit coupling effects as the spin-orbit parameter is only 100 cm^{-1} for divalent iron and furthermore only splits the ^5E_g upper state in second order.[1]

The splitting could arise from noncubic crystal fields at the ferrous ion site. These noncubic fields will be considered later, but are, in any case, not applicable to the cubic $MgO{:}Fe^{2+}$ and the nearly cubic $KMgF_3{:}Fe^{2+}$ and $KFeF_3$ crystals which also display a large splitting.

The splitting of these "cubic" crystals is due to dynamic Jahn-Teller effects of the type discussed by Longuet-Higgins *et al.*[2] and Liehr and Ballahusen.[3]

It is the purpose of this paper to describe the optical measurements made on various divalent iron compounds and to discuss the relevant effects of crystal-field symmetry on the apparent splittings.

EXPERIMENTAL DETAILS AND RESULTS

The optical absorption spectra of crystals of ferrous fluoride (FeF_2), potassium ferrous fluoride ($KFeF_3$), potassium magnesium fluoride doped with about 1% divalent iron ($KMgF_3{:}Fe^{2+}$), ferrous fluosilicate ($FeSiF_6{:}6H_2O$), anhydrous ferrous chloride ($FeCl_2$), and magnesium oxide doped with divalent iron ($MgO{:}Fe^{2+}$) were measured at 20, 77°K, and room temperature on a Unicam SP700 spectrophotometer. Low-temperature spectral measurements were made using a Dewar similar to the designs of Duerig and Mador[4] and Geiger[5]; cooling of the crystals is by thermal contact of these with a copper block, the latter being in contact with the liquid refrigerant. The crystal temperature was within 10°K of the refrigerant.

The splittings observed for the various crystals are listed in Table I, while Fig. 1 shows the absorption-band contour for $KMgF_3{:}Fe^{2+}$ whose absorption is characteristic of the "cubic" crystals. Splittings of the same type as given here have previously been reported by Cotton and Meyers[6] and Holmes and McClure[7] who give the splitting for $Fe(H_2O)_6{}^{2+}$ in aqueous solu-

TABLE I. Frequencies of the quintet-quintet optical transitions for various compounds of divalent iron.

Compound	Temperature (°K)	Mean frequency of the absorption band (cm^{-1})	Splitting (cm^{-1})
FeF_2	290	8800	3600
	77	9050	3500
	20	9150	3500
$KFeF_3$	290	8700	2200
	77	9100	2150
	20	9100	2150
$KMgF_3{:}Fe^{2+}$	290	9250	1800
	77	9500	1400
	20	9500	1350
$FeSiF_6 \cdot 6H_2O$	290	9700	1400
	77	10 700[a]	...
	20	10 700[a]	...
$FeCl_2$	290	7000	1400
	77	7400	800
	20	7350	700
$MgO{:}Fe^{2+}$	290	10 300	1800
	77	10 900	1400
	20	10 850	1300

[a] No clearly resolved doublet structure.

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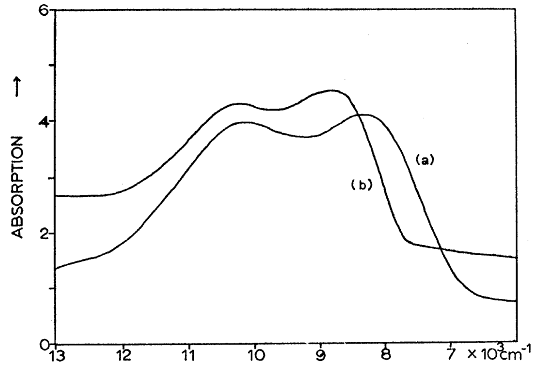

FIG. 1. Optical absorption of $KMgF_3:Fe^{2+}$. Curve (a) is the room-temperature spectrum; curve (b) is the 77°K spectrum. The 20°K spectrum is very similar to the 77°K one and is not shown. The two curves are displaced vertically relative to each other for clarity. The units on the ordinate are arbitrary.

tion, for ferrous ammonium sulphate, and for ferrous fluosilicate as 2100, 2400, and 1600 cm^{-1}, respectively. Similar data are also presented by Cotton and Meyers[6] on the analogous spectra of Co^{3+} in the double fluorides. Low-temperature measurements have been made on ferrous fluosilicate by Agnetta *et al.*[8] who finds no splitting for this compound, but only an asymmetric absorption band.

The undiluted divalent iron compounds show additional absorption bands at higher energies arising from transitions to excited triplet states. These bands are considerably weaker than the main band in the near infrared. They show considerable structure especially at low temperatures due to coupled lattice vibrations. Although these absorption bands are of intrinsic interest in themselves, they do not form part of the subject of this paper so will not be discussed further here.

DISCUSSION

The theorem of Jahn and Teller[9] states that electronically degenerate states of nonlinear molecules are unstable with respect to certain asymmetric displacements of their nuclei and will tend to distort in such a way as to remove the electronic degeneracy. If the stability attained by assuming an asymmetric nuclear configuration is no more than the zero-point energy of a typical vibrational mode, a special coupling between the electronic and nuclear motions will occur. These interactions constitute the dynamical Jahn-Teller effect. Longuet-Higgins *et al.*[2] have considered the simple model of a doubly degenerate vibration. It displays the essential features of the dynamic John-Teller effect. Using this model Longuet-Higgins *et al.* show that, for a vibronic transition from a singlet ground state to a doubly degenerate upper state, the envelope of the absorption band shows two intensity maxima (see Fig. 4 of Ref 2). The optical transition of divalent iron corresponds to this vibronic transition so the double peaked absorption band experimentally observed is qualitatively explained.

Of the ferrous compounds studied here, only the $MgO:Fe^{2+}$, $KMgF_3:Fe^{2+}$, and $KFeF_3$ have crystal cubic symmetry. All the rest are either orthorhombic (FeF_2) or trigonally distorted ($FeCl_2$, $FeSiF_6 \cdot 6H_2O$). Electron spin-resonance measurements by Low and Weger[1] show that divalent iron in magnesium oxide is situated at a cubic symmetry site in the lattice. Similar electron spin-resonance experiments on the $KMgF_3:Fe^{2+}$ crystals by Hall[10] failed to reveal spin-resonance absorption due to divalent iron. It is concluded that this crystal is distorted sufficiently to prevent observation of the electron spin resonance spectrum. Wyckoff[11] gives the symmetry as monoclinic ($a=b=c=8.00$ Å, $\beta=91°18'$). $KFeF_3$ has the ideal cubic perovskite structure at room temperature ($a=4.122\pm0.001$ Å), but distorts to become rhombodhedral ($a=4.108\pm0.002$ Å) at 78°K.[12] Thus the splittings observed in $MgO:Fe^{2+}$ and in room-temperature $KFeF_3$ are the only ones representative of divalent iron in sites of pure cubic symmetry.

The quantitative explanation of the observed splittings in these cubic compounds has been given by O'Brien,[13] who shows that the crystal-field model can account for the observed values to within a factor of 2 and that the remaining discrepancy may be attributed to the deficiencies of the model and to the approximation of the crystal lattice spectrum to the Debye model.

Of the noncubic compounds, those with a tetragonally distorted ferrous ion site show a larger splitting and those with a trigonally distorted ferrous ion site show a smaller splitting than the "cubic" compounds. The larger splitting of the "tetragonal" compounds (represented here by ferrous fluoride, and by ferrous ammonium sulphate in the data of Cotton and Meyers[6]) comes from the first-order splitting of the upper E_g state by the orthorhombic crystal field. The presence of this low-symmetry splitting is shown in the ferrous fluoride by the partial and opposite polarization of the two components of the absorption band; it is doubtful whether there would be any Jahn-Teller effect operating in this low-symmetry substance. One cannot invoke low-symmetry trigonal fields to account for the corresponding splitting of the trigonal ferrous compounds, because these fields do not split the upper E_g state in first order. The behavior of the splittings in this

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case has been considered by Vekhter[14] who applied his analysis to the data of Cotton and Meyers[6] on aqueous Fe^{2+} and the fluosilicate, and to data by Pappalardo[15] on Cu^{2+} in fluosilicates. Vekhter attributes the splitting of the absorption band to the relative symmetry of the minima displayed by the potential surfaces for the excited and ground electronic states as a function of of normal coordinates Q of the octahedron.[16] Both the E_g excited state and the T_{2g} ground state are unstable in a configuration of true octahedral symmetry; the degeneracy of these levels is lowered by distortions of the octahedral symmetry. These distortions are described by normal vibrations e_g, etc. For the excited E_g state the potential surface (as a function of normal coordinates Q_2 and Q_3) has three tetragonal minima, while for the T_{2g} ground state the potential surface displays these same three minima and also four trigonal minima in the normal coordinates Q_4, Q_5, and Q_6 arising from a t_{2g} vibration. If the ground and excited states have the same symmetry, a splitting of the absorption band results; if the symmetries differ, a single absorption band is expected. In the case of divalent iron spectra, one obtains a splitting of the main absorption band if the tetragonal minima of the T_{2g} ground state lie below those of the trigonal. An expression for the magnitude of the splitting is given by Vekhter and yields values of splittings substantially smaller for trigonal symmetry crystals because the trigonal field reduces the Jahn-Teller distortion in the ground state. The model thus qualitatively appears to explain the reduced magnitude for the band splitting in trigonal ferrous compounds. However, this model seems to be inconsistent with the conclusions of Van Vleck[17] and O'Brien[14] who show that the Jahn-Teller effect is much larger in the E_g upper state (by at least ten times) than that in the T_{2g} state. The Jahn-Teller distortion of the ground state must be very small as evidenced by the electron spin-resonance measurements on $MgO:Fe^{2+}$.[1] Consequently the model of Vekhter seems invalid, as it postulates the reduced splittings in trigonal compounds as due to a reduction in a Jahn-Teller splitting in the ground state.

For the trigonal compounds, one must consider the effect of the trigonal crystal field on the T_{2g} ground state. This has been given by Jackson[18] for ferrous fluosilicate. The $^5T_{2g}$ level is split by the trigonal field by an amount[19] $d = 1200$ cm^{-1} into two levels; the lower of these is further split by spin-orbit coupling into five levels, namely a singlet lowest and two doublets at energies e and $4e$ above this singlet where $e = 10.9$ cm^{-1}.[20] The lower trigonal field level corresponds to an orbital singlet and will not be Jahn-Teller split; the upper trigonal field level is too far away (1200 cm^{-1}) from the ground state to be populated sufficiently to influence the absorption spectrum of the crystal. Hence the system appears to reduce to the "cubic" crystal type with a negligible Jahn-Teller distortion in the ground state. It seems that, as in the cubic compounds,[13] the dominant Jahn-Teller distortion is in the excited state, and no splitting of the ground state (either by Jahn-Teller or by low-symmetry field) can be wholly responsible for the observed variations in the band separation with crystal symmetry. The effect of the low-symmetry field on the ground state will be partially quenched,[19] in any case, if the Jahn-Teller effect is present in sufficient strength. The action of the trigonal field on the excited-state Jahn-Teller distortion appears to be the reason for the reduced band separations in trigonal compounds.

The temperature dependence of the splittings is another aspect whose interpretation is uncertain. Presumably a similar mechanism as used for the "cubic" crystals,[13] viz. a greater spread in the ground state in Q space due to increased population of higher vibrational states, also applies in the trigonal compounds with the additional possible occurrence of low-lying electronic levels formed by the action of the trigonal field contributing to the high-temperature absorption spectrum. The temperature dependences are more marked than in the "cubic" compounds, and at 300°K the band separations approach those for the "cubic" crystals.

This paper presents the experimental data obtained; further analysis of these must await additional experimental and theoretical information on the divalent iron system.

SUMMARY

Data have been presented on the splittings of the main absorption band of divalent iron for several crystal compounds.

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