Jahn-Teller effects for Fe^{2+} in a $KZnF_3$ crystal

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Electron-paramagnetic-resonance and far-infrared investigations on the $(FeF_6)^{4-}$ complex in $KZnF_3:Fe^{2+}$ are presented together with a consistent explanation of the observations using the model proposed by Ham, Schwarz, and O'Brien [Phys. Rev. 185, 548 (1969)].

In-this paper we present electron-paramagnetic-resonance (EPR) and far-infrared (FIR) investigations on the $(FeF_6)^{4-}$ complex in $KZnF_3:Fe^{2+}$.

The problem of a d^6 configuration in a crystal field of cubic symmetry and octahedral coordination is of particular interest. The energy-level scheme as given by crystal-field theory is such that the lowest energy level is a 15-fold degenerate state $({}^5T_{2g})$. If the perturbation of the spin-orbit interaction is taken into account, the $({}^5T_{2g})$ level splits up into a number of states of which a Γ_{5g} triplet is the lowest, and the first excited states, Γ_{3g} and Γ_{4g} (separated by a few cm^{-1}) are predicted to lie at an energy approximately $-2\lambda \approx 200\ cm^{-1}$ above Γ_{5g}.[1] Since the ground state is degenerate, the Jahn-Teller (JT) theorem predicts that the complex would deform itself in order to remove this degeneracy.

The JT effects manifest themselves primarily as reductions of the effective spin-orbit splitting and of the orbital contribution to the magnetic moment.

As simultaneous experimental information about magnetic properties of ground-state triplets and the position of their first excited levels is very scarce at the present time, the results of this investigation may furnish data relevant to this problem. It is then the purpose of this work to provide EPR data of the ground state, to locate in the FIR region the position of the first excited levels, and to attempt to offer a consistent explanation of the observations, using the model proposed by Ham, Schwartz and O'Brien (HSO).[2]

The $KZnF_3$ single crystals used in this experiment were grown from the melt with a nominal concentration of 0.2% of Fe. The EPR measurements were performed at low temperatures (20 K to 2.4 K) with a conventional 35 GHz spectrometer. The FIR measurements were obtained at 4 K using an FT spectrometer.

The observed EPR spectrum (Fig. 1) exhibited three important features: (i) a strain-broadened isotropic line I (on the left of Fig. 1) with a g value around 3.4; (ii) a sharp isotropic line II (arrow) superimposed on the first, the center of which is shifted ($g = 3.46$) to a lower magnetic field not coinciding with the center of line I. A peculiar feature of line II is that it has a phase which is inverted with respect to that of line I and corresponds to a reduction in the net absorption of microwave power; and (iii) a very asymmetric isotropic line III (on the right of Fig. 1) with apparent g value of 6.8.

The appearance of some of these features has been previously observed for Fe^{2+} in $KMgF_3$ and MgO,[1,3] and can be interpreted as follows: The broad line I is attributed to the $\Delta M_s = \pm 1$ transition between the three states of the Γ_5 ground triplet. Broadening is due to local lattice strains.[4] Line II corrsponds to transitions of sites experiencing minimum strain. Sites where the strain shift of spin packets is smaller than their width exhibit self-cross relaxation and are the only ones to contribute to line II.[4] The fact that the center of the broad line is shifted to a higher magnetic field can be explained as a significant distortion of the line shape occurring when the linewidth is comparable to the value of the magnetic field at resonance.[5] Line III appears at half field (i.e., $g \simeq 6.8$) and corresponds to forbidden $\Delta M_s = \pm 2$ transitions of the ground triplet. This line has a shape similar to that of the Fe^{2+}:MgO half-field line considered in detail by McMahon.[6]

The ground-state triplet can be described by a Zeeman spin Hamiltonian with an effective spin $S = 1$ and a g value of 3.46 as estimated from the center of the inverted phase line II. Departure of the experimentally found g value 3.46 from the calculated crystal field value[1] ($g = 3.53$) may be attributed to covalency or JT effects. Evaluation of the superhyperfine interaction of the ferrous ion with its neighbors in a similar environment[3] ($Fe^{2+}:KMgF_3$) indicates that covalency does not contribute significantly to a g-value reduction; thus the JT effect is expected to account for the above mentioned reduction.

The JT calculations for these cases have been developed by Ham, Schwarz, and O'Brien[1] and successfully applied to explain JT effects in the FIR, EPR, and Mössbauer spectra of $MgO:Fe^{2+}$.

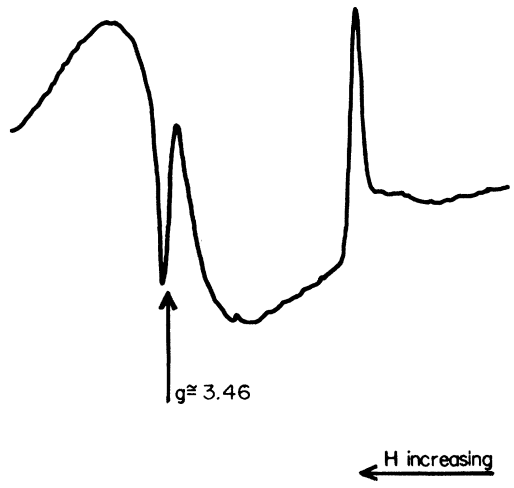

FIG. 1. $KZnF_3:Fe^{2+}$ EPR spectrum (4 K), $\nu = 35$ GHz.

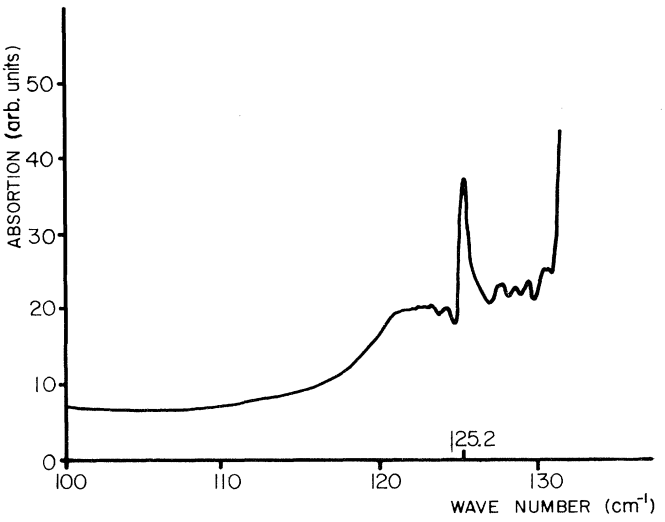

FIG. 2. Fourier-transform far-infrared spectrum of $KZnF_3:Fe^{2+}$ at 2 K.

The expression for the g value obtained by HSO[1] is given by

$$g=(g_s^0-8\lambda/\Delta)K_s-KK_L-(2\lambda/\Delta)K_A+(12\lambda/\Delta)K_B\ldots\ , \tag{1}$$

where Δ is the crystal field splitting, λ the free-ion spin-orbit interaction parameter, $g=2.0023$, the free-spin g value, K the orbital reduction factor and K_s, K_L, K_B, are JT reduction factors.[1] We refer the reader to the HSO paper[1] for the explicit formula of these factors. It is sufficient to mention here that they depend on the effective angular frequencies (ω_E and ω_T) of the local E_g and T_{2g} lattice modes of distortion and on the JT coupling energies ($E_{\rm JT}^E$ and $E_{\rm JT}^T$) for these modes.

It is important, as we shall see, to calculate the latter mentioned energies ($E_{\rm JT}^E$ and $E_{\rm JT}^T$) in order to obtain the position of the first excited (Γ_{3g} and Γ_{4g}) levels.

For this purpose we use Eq. (1), making the following assumptions: The cubic field splitting Δ is taken to be 9500 cm^{-1}, following optical absorption measurements on $(FeF_6)^{4-}$ by Jones;[7] λ is assumed to have the free-ion value of 100 cm^{-1}; covalency is neglected, and therefore $K=1$.

To obtain values for the JT reduction factors it is necessary to know the angular frequencies of the local modes (ω_E and ω_T). These are expected to be different from the pure lattice modes because Fe replaces Zn in the lattice. Nevertheless, an estimate of the local mode frequencies when ^{53}Cr replaces ^{25}Mg in a similar perovskite ($KMgF_3$) has been made by Guha and Lange.[8] Their estimate for the frequencies was around 400 cm^{-1}. Since ^{56}Fe and ^{53}Cr are of nearly equal masses, we shall adopt these estimates for the present case.

Finally, we shall follow Ray and Regnard's[9] findings. These authors conclude, based on the Mössbauer spectra of $(FeF_6)^{4-}$ in a similar lattice ($KMgF_3$) under an applied high-magnetic field, that coupling to the T_{2g} modes dominates. The same conclusion is reached by Kim and Lange[10] from features observed in acoustic relaxation measurements on $Fe^{2+}:KMgF_3$. We have calculated the $E_{\rm JT}^T$ energy for a local mode frequency of 400 cm^{-1}. Using this assumption ($E_{\rm JT}^E=0$), the obtained value is $E_{\rm JT}^T=106$ cm^{-1}. It is important to mention that $E_{\rm JT}^T$ is not very sensitive to the choice of frequency.

Using the obtained $E_{\rm JT}^T$ value and the appropriate formula given in the HSO paper,[1] it is possible to predict the position of the first excited levels. Our calculations turn out to be 145 cm^{-1} for the $\Gamma_5\rightarrow\Gamma_4$ transition and 129 cm^{-1} for the $\Gamma_5\rightarrow\Gamma_3$ transition.

Fourier transform FIR measurements at 4 K (Fig. 2) show a line at 125 cm^{-1}. Following application of an external magnetic field to the sample, the 125 cm^{-1} line gradually shifts to 127 cm^{-1} at 8 T. We may then assume that this line corresponds to $\Gamma_5\rightarrow\Gamma_3$ transition.

As predicted by the above results the second excited level (145 cm^{-1}) may probably be buried in the $KZnF_3$ phonon region (between 129 and 150 cm^{-1}), making its observation difficult.

From this we conclude that the model proposed by HSO[1] consistently explains the behavior of $(FeF_6)^{4-}$ in $KZnF_3$.

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