

## Acoustical relaxation due to the ferrous ion in $\text{KMgF}_3$

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An acoustical relaxation absorption in  $\text{KMgF}_3$  is identified as due to ferrous impurities. A variety of pure acoustical modes are used to determine the symmetry and magnitude of the vibronic coupling of the acoustic wave with the impurity. Coupling of  $T_{2g}$  distortions is observed to dominate the relaxation process. From analysis of the frequency and temperature dependence of the acoustical relaxation process an excitation energy of  $94 \text{ cm}^{-1}$  is obtained for the ferrous ion and is identified as due to the spin-orbit splitting of the ground state. This spin-orbit splitting is below the crystal-field value, and it is assumed the reduction is due to a dynamic Jahn-Teller effect. These results agree with electron-paramagnetic-resonance studies on the same samples.

### INTRODUCTION

The attenuation of an acoustical wave propagating in a crystalline solid includes contributions due to phonon-phonon interactions occurring in the perfect lattice as well as to scattering from impurities and imperfections. This latter contribution can exhibit a characteristic temperature dependence when resonance scattering leads to a relaxation absorption in the acoustical attenuation. Identification of relaxation absorption with a particular impurity often provides information about the low-lying excitations of the impurity and its environment. The assignment of energy levels can proceed more readily if the relaxation absorption can be characterized by a single-relaxation-time Debye process.

The coupling of the acoustical wave to the electronic states of the impurity occurs as a result of degeneracies which are lifted as a result of local distortions of crystal-field symmetry induced by the harmonic acoustical-wave train. Since the acoustical wave propagates for the most part in a perfect lattice when not interacting with the impurity, the atomic strains are known for the pure acoustical modes of the host lattice used in this investigation. It is then possible to devise a set of strain selection rules<sup>1</sup> whose fulfillment is a necessary condition for interaction with the electronic ground state of the impurity. Although conformity to these strain selection rules is a necessary condition for interaction with the impurity it is not sufficient to guarantee interaction. The sufficiency of interaction depends not only on the symmetry of the strain and electronic states but the magnitude of the coupling strength.

In this investigation, observation of acoustical relaxation absorption is used to discern the low-lying ( $<100 \text{ cm}^{-1}$ ) excitation spectrum of the ferrous ion in the  $\text{KMgF}_3$  spectrum. The magnitude

of the observed relaxation absorption offers a qualitative indication of the strength of the coupling constants of the various phonon modes to the ferrous-ion impurity.

The electronic term of the ferrous ion is a five-fold degenerate triplet ( ${}^3T_{2g}$ ) in a cubic crystal field. This is further split by spin-orbit interactions into a triplet ground state ( $T_{2g}$ ) with two closely spaced excited states ( $E_g$  and  $T_{1g}$ ) at an energy of  $-2\lambda$  according to crystal-field theory, where  $\lambda$  is the free-ion spin-orbit parameter ( $\sim 100 \text{ cm}^{-1}$ ). The observed spin orbit splitting is considerably less than this value; infrared absorption measurements are ambiguous as to the magnitude of the spin orbit splitting. These values vary from<sup>2</sup>  $87 \text{ cm}^{-1}$  to less than<sup>3</sup>  $52 \text{ cm}^{-1}$ .

The magnitude of the spin-orbit splitting is important in that it indicates the extent to which the observed value is reduced below the crystal field value ( $2\lambda \approx 200 \text{ cm}^{-1}$ ) by covalency and the dynamic Jahn-Teller effect. A similar reduction in the spin-orbit splitting is observed for  $\text{Fe}^{2+}$  in  $\text{MgO}$ ,<sup>4</sup> where the reduction due to covalency is estimated to be only 10%. Assuming a similar value for  $\text{Fe}^{2+}$  in  $\text{KMgF}_3$  would imply that the dynamic Jahn-Teller effect is dominant in reducing the spin-orbit splitting. Although some of the infrared measurements on  $\text{KMgF}_3 : \text{Fe}^{2+}$  indicate a large reduction in spin-orbit interaction with a correspondingly large Jahn-Teller energy, electron paramagnetic measurements<sup>5</sup> favor a smaller Jahn-Teller reduction more in line with that observed for  $\text{Fe}^{2+}$  in  $\text{MgO}$ .

### EXPERIMENTAL ARRANGEMENT

The acoustical attenuation is measured using a pulse-echo method at hypersonic frequencies. Measurements are made at two frequencies (1 and 3 GHz) and over a wide temperature range (1.5 to  $150 \text{ }^\circ\text{K}$ ). The samples are in the form of a rec-

tangular parallelepiped with two plane parallel polished faces which are oriented perpendicular to either the [100] or [110] directions to produce pure lattice modes. The acoustic wave is generated by a resonant quartz disc fixed to the sample by a thin layer of silicone oil (200 cS). The piezoelectric quartz disc is placed in a high electric field point in a reentrant microwave cavity. The  $\text{KMgF}_3$  crystals are grown in our Crystal Growth Facility and doped to prescribed levels with ferrous ions which substitute for magnesium ions in the  $\text{KMgF}_3$  lattice. The impurity levels are determined by atomic absorption.

To identify the acoustic relaxation absorption due to the ferrous ion an undoped crystal is measured as a function of temperature to obtain the attenuation due to phonon interaction in the host lattice and the scattering due to imperfections. Samples which contain different impurity levels of the ferrous ion are then measured. The relaxation peak which is observed as a maximum above a constant background when the ferrous ion is present must scale in height linearly with the impurity concentration. As seen in Fig. 1 these relaxation-absorption heights scale with the impurity concen-

tration. The background attenuation (taken as the average value at the lowest temperatures) also increases with increasing impurity concentration, indicating an increase in imperfections with impurity concentration. This is reasonable since the ionic radius of the ferrous ion is larger than the magnesium for which it substitutes. Internal strains are expected to be larger with a higher impurity concentration; this is verified by electron-paramagnetic-resonance measurements. The major uncertainty in scaling the magnitude of the relaxation peaks is in the determination of the impurity concentration.

#### SYMMETRY AND STRAIN-COUPLING STRENGTH

Scattering of acoustical energy by the impurity system leads to attenuation of the acoustical wave and is a result of the interaction of the wave with the electronic states of the impurity. The harmonic strain of the acoustic wave perturbs the local crystal field symmetry; it can reduce the degeneracy of the electronic states of the impurity, and leads to a coupling of the acoustical wave to the electronic system. The particular symmetry of the acoustical strain distribution and the impurity's electronic ground state determine whether an interaction is possible. The strength of the coupling is reflected in the magnitude of the relaxation maximum and is considered an empirical parameter.

The necessary condition for the interaction of the acoustical wave with the impurity system can be phrased in terms of a strain selection rule using the methods of group theory. Physically the model assumes that the local distortions of the lattice of the ferrous impurity and its six octahedrally coordinated fluorine nearest neighbors can be decomposed in terms of the normal modes of an octahedral molecule. This approach is consistent with the interpretation of the dynamic Jahn-Teller effect which assumes coupling to local distortions classified in terms of the octahedral cluster modes. Those normal modes which reduce the symmetry of the crystal enough to either remove a degeneracy or change the relative positions of the electronic energy levels can also lead to acoustical scattering. The normal modes which couple with the ferrous electronic ground state correspond to strains of tetragonal ( $E_g^e$ ), orthorhombic ( $E_g^e$ ) and a combination of linear and angular distortions ( $T_{2g}^e$ ). All these normal modes lower the local crystal-field symmetry such that the degeneracy of the  $T_{2g}^e$  electronic ground state is removed and an interaction with these acoustic modes is allowed by symmetry.

For the attenuation measurements only pure

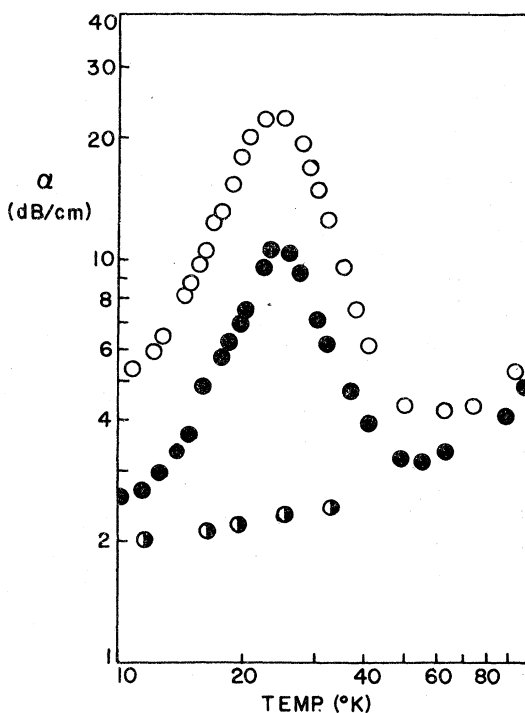


FIG. 1. Attenuation coefficient ( $\alpha$ ) for the fast transverse ( $c_{44}$ ) acoustical mode in  $\text{KMgF}_3$  containing three different concentrations (O—9200 ppm, ●—4000 ppm, ◐—30 ppm) of ferrous impurities. The measurement frequency is 1 GHz and propagation is along the [100] direction.

TABLE I. Irreducible representations and elastic stiffness moduli for some pure longitudinal ( $L$ ) and transverse ( $T$ ) modes in a cubic crystal. The subscripts indicate the propagation direction and the superscripts indicate the polarization direction.

Mode	Stiffness moduli	Irreducible representations
$L_{100}$	$c_{11}$	$A_{1g} + E_g^0$
$L_{110}$	$\frac{1}{2}(c_{11} + c_{12} + 2c_{44})$	$A_{1g} + E_g^0 + T_{2g}$
$L_{111}$	$\frac{1}{3}(c_{11} + 2c_{12} + 4c_{44})$	$A_{1g} + T_{2g}$
$T_{100}^{001}$	$c_{44}$	$T_{1g} + T_{2g}$
$T_{110}^{100}$	$c_{44}$	$T_{1g} + T_{2g}$
$T_{110}^{110}$	$\frac{1}{2}(c_{11} - c_{12})$	$A_{2g} + E_g^e + T_{1g}$
$T_{111}^{111}$	$\frac{1}{2}(c_{11} - c_{12} + c_{44})$	$E_g + T_{1g} + T_{2g}$

acoustical modes of the host lattice are used; this means that the lattice distortions are known on an atomic level. The strain symmetries of the pure acoustical waves for various polarizations (transverse  $T$  and longitudinal  $L$ ) can be written in terms of the irreducible representations of the cubic group in Table I; the pure modes labeled by their polarization and propagation directions are given with their stiffness constants in terms of their irreducible representations. As can be seen from this table, all the pure modes may satisfy the necessary condition for interaction with the ferrous impurity since they all contain at least one of the degeneracy-reducing irreducible representations ( $E_g^0$ ,  $E_g^e$ , and  $T_{2g}$ ).

The empirical results indicate a considerable variation in the magnitude of the interaction. The relaxation absorption which is indicative of the strength of the interaction is almost completely missing for one of the pure lattice modes. The longitudinal propagation along the [100] direction does not exhibit an appreciable relaxation absorption, although for a transverse mode along the same direction, a relaxation absorption is clearly seen. In Fig. 2 the temperature dependence of the acoustical attenuation for three pure acoustical modes indicates a clear relaxation maximum for only two of the modes. However, all three modes fulfill the necessary condition for interaction with the impurity, i.e., their irreducible representations contain either the  $E_g^0$ ,  $E_g^e$ , or  $T_{2g}$  mode. The common feature of the irreducible representations for the modes which do exhibit a relaxation maximum are that they contain the  $T_{2g}$  irreducible representation. This implies that the magnitude of the coupling to the  $T_{2g}$  distortions of the octahedral cluster is much greater (>20 times) than the

coupling to the purely linear distortions ( $E_g$ ). This result suggests that quenching of the spin-orbit interaction by the dynamic Jahn-Teller effect is predominantly through the  $T_{2g}$  local distortion rather than both  $T_{2g}$  and  $E_g$ . This is contrary to what had been implied previously by Ray *et al.*<sup>3</sup> from the ratio of the magnetoelastic coupling constants. Mössbauer studies on  $\text{KMgF}_3$  by Regnard *et al.*<sup>6</sup> also indicate a dominant  $T_{2g}$  coupling. In the following, the spin-orbit quenching by the dynamic Jahn-Teller effect is assumed to occur through the  $T_{2g}$  local mode.

#### RELAXATION ABSORPTION

The acoustical wave couples to the impurity ion by virtue of a dynamic strain splitting of the ions' electronic states. This interaction is dynamic in that the acoustical strain is varying at a rate equal to the acoustical frequency, and the impurity is making transitions between electronic states through excitations from lattice thermal phonons. Both the impurity and its neighbors are involved in the transitions between vibronic states. The

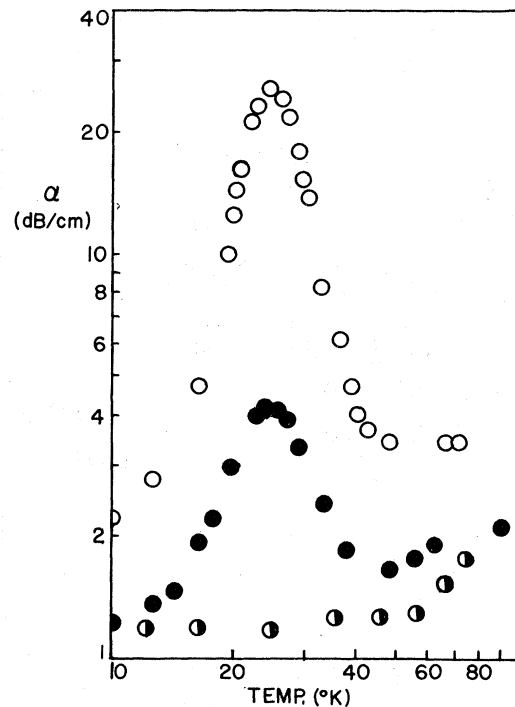


FIG. 2. Attenuation coefficient for three different acoustical modes propagating in  $\text{KMgF}_3$  containing 4000 ppm ferrous impurity. The fast transverse ( $\circ$ ) and longitudinal modes ( $\bullet$ ) propagate along the [110] direction while the other longitudinal mode ( $\odot$ ) propagates along the principle axis direction [100]. The measurement frequency is 1 GHz.

acoustical wave is then interacting with a local environment which is varying in time, and the scattering of the acoustical wave can be characterized as dynamic. The magnitude of the acoustical attenuation depends on both the strength of the strain coupling and the rate of vibronic transitions relative to the acoustical frequency. The maximum attenuation occurs when the radial acoustic frequency ( $\omega$ ) and the reciprocal of the transition rate ( $\tau$ ) are equal.<sup>7</sup> The transition rate is proportional to the number of lattice phonons with energy large enough to excite the impurity between vibronic states. The transition rate is assumed to be given by the Orbach<sup>8</sup> rate  $\tau^{-1} = \tau_0^{-1} e^{-\Delta/RT}$  for indirect transitions. This rate increases as the temperature increases so the maximum in the position of the relaxation absorption ( $\omega\tau = 1$ ) depends on the acoustical frequency. In Fig. 3, the position of the relaxation maximum occurs at a lower temperature for a 1-GHz acoustical wave than for a 3-GHz wave. From the positions of these two maxima and knowledge of the acoustical frequencies, the coefficient  $\tau_0$  and indirect transition energy  $\Delta$  can be determined.

The shape of the relaxation absorption is de-

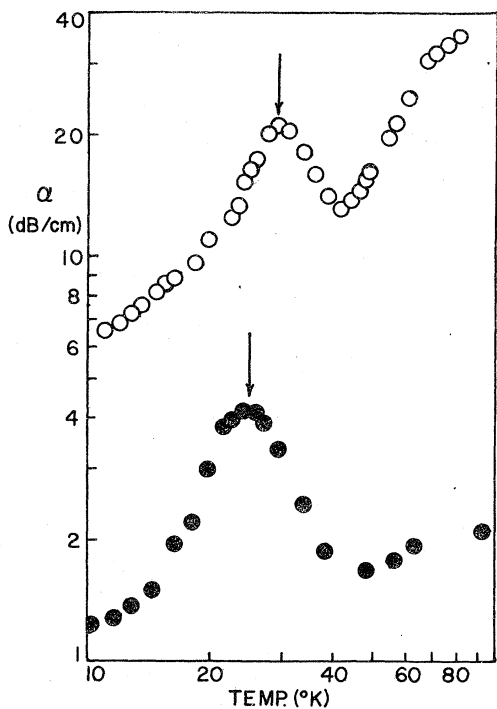


FIG. 3. Attenuation coefficient for the longitudinal mode propagating along the [110] direction in  $\text{KMgF}_3$  containing 4000 ppm ferrous impurity. The temperature at which the relaxation is a maximum is indicated by an arrow for both the 1 GHz ( $\bullet$ ) and 3 GHz ( $\circ$ ) measurements.

termined by the distribution of relaxation times. If only one relaxation process is present, the shape of the peak is a function of temperature and can be described phenomenologically by a simple Debye relaxation absorption. The peak shape is given by

$$\alpha = \alpha_0 \omega \tau / (1 + \omega^2 \tau^2). \quad (1)$$

Using the parameter  $\tau_0$  and  $\Delta$  determined from Fig. 3, the shape reconstructed using Eq. (1) is consistent with a single relaxation mechanism. This latter result makes it plausible to associate the parameter indirect transition energy ( $\Delta = 94 \text{ cm}^{-1}$ ) determined for a relaxation absorption of the ferrous ion with the low-lying energy levels of this ion.

The interpretation of the temperature and frequency dependence of the acoustic relaxation suggests an excited energy level  $94 \text{ cm}^{-1}$  above the ground state for the ferrous ion. Measurements on the temperature dependence of electron paramagnetic resonance spectra also indicate an excited state  $94 \text{ cm}^{-1}$  above the ground state.<sup>5</sup> This energy level is assumed in the following to be due to first excited electronic states ( $T_g^e$  and  $E_g^e$ ) of the ferrous ion. This conflicts with interpretations of some far infrared absorption measurements.<sup>3</sup> An infrared absorption associated with the ferrous ions is observed in this energy range but due to either unusual magnetic field<sup>9</sup> or concentration dependencies<sup>3</sup> it is assumed not to be due to electronic transitions of the ferrous ion. The coincidence of the acoustical relaxation excitation level and that determined from EPR measurements<sup>5</sup> (including the magnitude of the  $g$  factor) indicates the  $94 \text{ cm}^{-1}$  is associated with the first electronic excited state.

Crystal-field theory predicts the separation of the ground and first excited state to be approximately  $190 \text{ cm}^{-1}$ . This is considerably larger than the observed value of  $94 \text{ cm}^{-1}$  and indicates a substantial reduction in the spin-orbit interaction over the crystal-field model. A reduction in spin-orbit interaction may also result from covalent bonding of the ferrous impurity and fluoride neighbors. Evaluation of the superhyperfine interactions of the ferrous ion<sup>10</sup> indicate it is unlikely that covalency with the fluorine would be significant enough to explain the rather substantial reduction in the spin-orbit splitting. The effect of covalency for the ferrous ion in MgO is determined by Ham, Schwartz, and O'Brien<sup>4</sup> to be less than 10% of the spin-orbit reduction and would be expected to be even less for  $\text{KMgF}_3 : \text{Fe}^{2+}$ .

Another mechanism for reducing the spin-orbit

splitting is the dynamic Jahn-Teller effect. This mechanism has been successfully applied by Ham, Schwarz, and O'Brien to explain the reduction in spin-orbit coupling of the ferrous ion in MgO. If the effects of covalency are ignored, an upper bound on the Jahn-Teller energy can be found for the  $\text{KMgF}_3:\text{Fe}^{2+}$  system. Assuming local-mode frequencies of  $300-400\text{ cm}^{-1}$  and coupling only to  $T_{2g}$  modes, a magnitude of  $108\text{ cm}^{-1}$  is obtained as an upper bound to the Jahn-Teller energy. This value leads to a reduced  $g$  factor which is consistent with the observed value obtained from EPR spectra<sup>5</sup> of the same samples as for the acoustical relaxation measurements.

#### SUMMARY AND CONCLUSION

The magnitude of the acoustical-relaxation peak indicates the strongest coupling is to a  $T_{2g}$  symmetry distortion. The frequency and temperature dependence of the relaxation absorption indicates a single relaxation process with an excitation energy of  $94\text{ cm}^{-1}$ . This energy is associated with the spin-orbit splitting of the ferrous ion which is reduced below the crystal-field value by the dynamic Jahn-Teller effect.

#### ACKNOWLEDGMENT

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