AVERAGING BY RELAXATION AND THE DYNAMIC JAHN-TELLER EFFECT

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Averaging effects produced by relaxation have been observed for $SrCl_2:La^{2+}$, a system exhibiting the dynamic Jahn-Teller effect. Observed temperature and sample dependences are consequences of a rapid direct relaxation process between the vibronic components of the ^2E ground state. This interpretation is consistent with similar effects seen for Cu^{2+}, Sc^{2+}, and Eu^{2+} in cubic crystals.

The first observation by electron paramagnetic resonance (EPR) of the dynamic Jahn-Teller effect was made on Cu^{2+} in sites of trigonal symmetry.[1] In order to explain the Cu^{2+} spectrum, Abragam and Pryce[2] suggested that an averaging process was occurring as a result of rapid reorientation of the complex consisting of the Cu^{++} ion and its neighbors between different possible static distortions. Their explanation was subsequently verified[3] by spectra exhibiting characteristics of a static Jahn-Teller effect at 20°K and below. Recently dynamic effects have been observed in EPR spectra even at liquid helium temperatures.[4-10] These spectra exhibit a cubic anisotropy, a characteristic line shape, and at temperatures near 10°K, an additional isotropic spectrum. The primary purpose of this Letter is to establish the origin of this isotropic spectrum which has previously been a subject of controversy.[4-11]

Two explanations have been advanced for both the anisotropic cubic-symmetry spectra and the isotropic spectrum. First, a strong-coupling theory developed by Bersuker,[12,13] and independently by O'Brien,[14] had been employed in interpretations by Coffman[4,5] (Cu^{2+} in MgO), Coffman, Lyle, and Mattison[6] (Cu^{2+} in CaO), Höchli and Estle[7] and Höchli[8] (Sc^{2+} in CaF_2 and SrF_2), and Chase[10] (excited ^2E state of Eu^{2+} in CaF_2 and SrF_2). The anisotropic spectra in these investigations were explained as a result of the system's ability to tunnel between energetically equivalent static distortions, while the isotropic spectrum was believed to arise from a population of the excited singlet level. An alternate explanation for both the isotropic and anisotropic spectra has been given by Ham[11] who considered a weakly coupled system and suggested that the isotropic spectrum could arise from "motional" averaging due to rapid relaxation.

Experiments on $SrCl_2:La^{2+}$ have enabled us to fit Ham's effective Hamiltonian description to within experimental accuracy.[15] We report here temperature- and sample-dependence measurements on $SrCl_2:La^{2+}$ which indicate that the isotropic spectrum results from averaging due to relaxation. This interpretation is not in agreement with previous arguments[4-8,10] assigning the isotropic spectrum to a populated excited singlet level.

Single crystals of $SrCl_2$ were grown from the melt by a vertical Bridgman technique with the lanthanum impurity introduced in the form of $LaCl_3$. In "as grown" samples, the divalent lanthanum charge state was not present in a concentration sufficient to produce detectable spectra at the highest available spectrometer sensitivies. By heating the crystals in strontium vapor[16] at approximately 600°C the La^{3+} ions could be reduced to form the desired La^{2+} impurity. Reduction times (the times during which the crystals were exposed to hot Sr vapor) were varied in the range from 5 to 45 min. EPR spectra of the reduced crystals were characteristic[11] of a ^2E state, implying that the La^{2+} ground-state configuration is $[Xe]5d^1$. This configuration has been identified previously[17] for $CaF_2:La^{2+}$ which exhibits the static Jahn-Teller effect. For La^{2+} in $SrCl_2$ the isotropic and anisotropic spectra coexisted (see Fig. 1) in the temperature range from 1.1°K to approximately 5°K. In the region near 6°K the anisotropic spectra became unde-

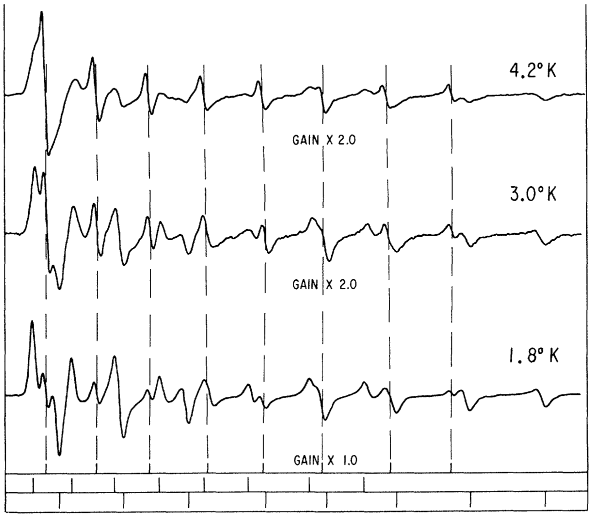

FIG. 1. Temperature dependence of the EPR spectrum at 8.9 GHz of $SrCl_2$:La^{2+} with $\vec{H}\|\langle 100\rangle$. The first derivative of absorption is shown versus magnetic field. The isotropic spectrum is located by dashed vertical lines.

tectable. The apparent intensities and line shapes of the remaining isotropic spectrum were dependent on the orientation of the applied magnetic field as evident from Fig. 2. The apparent intensity (the peak-to-peak amplitude in derivative presentation) of the isotropic spectrum increased as the field approached a $\langle 111\rangle$ direction. At each applied field orientation the isotropic low-field hyperfine line had the greatest apparent intensity, while the remaining hyperfine lines decreased in apparent intensity with increasing magnetic field.

A correlation of reduction time with intensity of the isotropic spectrum is shown in Fig. 3. For "long" reduction times [30 min as shown in Fig. 3(a)] the isotropic spectrum at a given temperature was more intense than for "short" reduction times [5 min as shown in Fig. 3(c)]. Figure 3(b) shows the isotropic spectrum obtained with an intermediate reduction time of 15 min. The temperature at which the isotropic spectrum appeared could be controlled to some extent by varying the reduction time and, in this connection, the isotropic spectrum in Fig. 3(c) could not be observed at 1.1°K while those in Figs. 3(a) and 3(b) could. When reduced for times in excess of 40 min the crystals fractured very easily, indicating the presence of large internal strains.

Rapid relaxation between certain levels of a system with an anisotropic spectrum can produce an averaging of the anisotropic components yielding an isotropic spectrum.[11,18-21] The condition for such an averaging is that the relaxation rate τ^{-1} (τ is not the spin-lattice relaxation time T_1) must satisfy the relation

$$\tau^{-1} \gg 2\pi\Delta\nu, \tag{1}$$

where $\Delta\nu$ is the difference in frequency between the two anisotropic components being averaged. For the case of a dynamic Jahn-Teller effect,

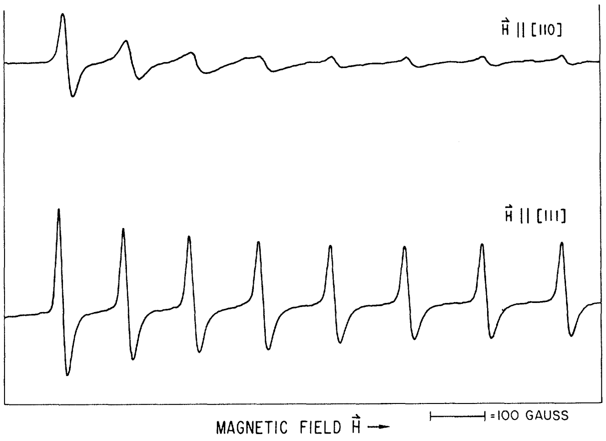

FIG. 2. Angular dependence of the isotropic EPR spectrum at 8.9 GHz of $SrCl_2$:La^{2+}. The first derivative of absorption is shown versus magnetic field.

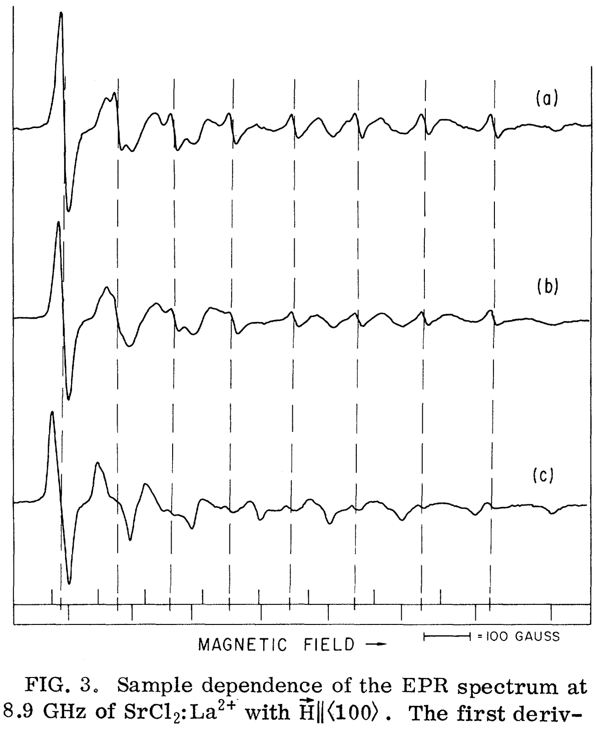

FIG. 3. Sample dependence of the EPR spectrum at 8.9 GHz of $SrCl_2$:La^{2+} with $\vec{H}\|\langle 100\rangle$. The first derivative of absorption is shown versus magnetic field. The isotropic spectrum is located by dashed vertical lines. (a) Reduction time 30 min. (b) Reduction time 15 min. (c) Reduction time 5 min.

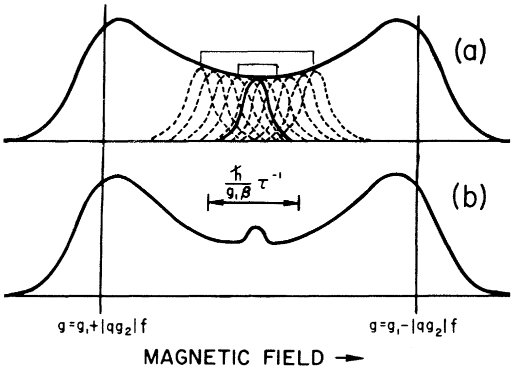

FIG. 4. The strain-produced EPR absorption line shape is shown (a) without and (b) with relaxation between vibronic levels. Note that the positions of the extrema vary with field direction via the factor $f=[1-3(l^2m^2+m^2n^2+n^2l^2)]^{1/2}$ where l, m, and n are the direction cosines of the magnetic field with respect to the cubic axes. The relaxation time for transitions between the strain-split vibronic levels is τ. Second-order terms which effect the line shape have been neglected.

random strains cause a characteristic first-order line shape [see Fig. 4(a)] which has been shown by Ham[11] to be the envelope of all possible transitions for the strain-split ^2E states occurring in pairs symmetrically placed about the center of the envelope. If there is a nonzero relaxation rate for the transition between strain-split states, the condition for averaging by relaxation is satisfied for some portion of the observed envelope, and one would expect averaging for just that portion [Fig. 4(b)]. The strain envelope varies as a function of applied field direction so that as the field approaches a ⟨111⟩ axis, the portion of the envelope satisfying Eq. (1) increases. Thus for this incomplete "motional" averaging one would expect the intensity of the isotropic line to increase as the field approaches a ⟨111⟩ direction. By similar arguments one would expect a variation among the hyperfine components at any field direction.

Ham[21] has discussed three possible relaxation mechanisms (a direct, a Raman, and an Orbach process) which could produce "motional" averaging. Each of these processes is characterized by a different temperature dependence. The intensity of the isotropic spectrum is approximately linear with temperature (see Fig. 1). This implies that the direct process is primarily responsible for the relaxation in this temperature region. Ham[21] has also shown that the direct-process relaxation rate increases as the square of the strain splitting δ between the ^2E-state components (if $\delta \ll kT$). This offers an explanation for the observed dependence of the intensity of the isotropic spectrum on reduction time, since for relatively long reduction times the crystals are apparently severely strained.

For $SrCl_2$:La^{2+}, as evidenced by our temperature- and sample-dependence studies, the isotropic spectrum results from averaging by relaxation of a portion of the anisotropic spectrum. The behavior of the isotropic spectra in other systems characterized by a dynamic Jahn-Teller effect at low temperature[4-8,10] is also consistent with this interpretation. Isotropic spectra observed for Cu^{2+}, Sc^{2+}, and Eu^{2+} may, of course, be due to one or more of the relaxation processes mentioned above.

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