

normal modes are now summations over the Brillouin zone, and the division of the summation as in Eq. (8) implies that we need only consider \vec{k} vectors in the reduced Brillouin zone. The eigenvector components $W_\alpha(\vec{k}|\vec{k}, p)$ and the eigenvalues

$[\omega(\vec{k}, p)]^2$ are found for such \vec{k} vectors using the matrices given by the MgO shell model of Peckham.⁹ The number of \vec{k} vectors which are to be included must be sufficient to make sampling errors unimportant.¹³

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EPR Spectrum of a Jahn-Teller System, NaCl:Cu⁺²

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The EPR spectrum of isolated Cu⁺² ions in NaCl obeys an axial spin Hamiltonian at low temperatures with $g_{||} = 2.373$, $g_{\perp} = 2.07$, $A_{||} = 95$ G, $A_{\perp} = 40$ G, $Q' = 20$ G with the z axis lying parallel to one of the cube edges. Upon warming toward room temperature, the ligand hyperfine spectrum disappears as the linewidth increases from 16 G at 4.2 K to 25 G at 77 K. At 95–100 K, as this spectrum disappears, a single isotropic line appears with $g = 2.16$ and a linewidth of 60 G. These low- and high-temperature spectra are interpreted as the static and dynamic Jahn-Teller distortions of the CuCl complex. A static strain experiment performed at 77 K results in a repopulation of the three distortion sites and enables a measurement of the strain coefficient V_2 to be made.

INTRODUCTION

As is well known, the ground state of the Cu⁺² ion ($3d^9$) in an octahedral field splits into a low-lying orbital doublet (E_g) and an excited triplet

(T_{2g}) separated by $10Dq$. Because of the ground-state orbital degeneracy, a Jahn-Teller (JT) distortion may occur that will remove the degeneracy and lower the energy of the complex (i.e., the ion and its surrounding ligands).¹ If frozen in this con-

figuration at low temperatures, the "static" JT effect, the system should be characterized by an axial spin Hamiltonian of the form

$$\mathcal{H} = g_z \beta H_z S_z + g_{\perp} \beta [H_x S_x + S_y H_y] + A I_z S_z + B [I_x S_x + I_y S_y] + Q' [I_z^2 - \frac{1}{3} I(I+1)], \quad (1)$$

while at high temperatures an isotropic or "dynamic" spectrum may result, since the given distortions are rapidly changing their orientation in a time short compared to that of the measurement. This present work gives the results of a set of measurements on NaCl:Cu²⁺ crystals that generally follow the prescription outlined above. In addition, a strain experiment was conducted on these crystals and a repopulation of the distortion sites was noted. This change in the population enabled an estimate of the strain coefficient to be made, as well as an independent check on the nature of the distortion, i.e., whether elongated or compressed.

For a more detailed theoretical description of the general problem of the EPR spectrum that results from a JT complex, the paper² and the review article³ by Ham should be consulted, as well as the references cited therein.

For application to the experimental results reported here on NaCl:Cu²⁺ one should additionally consult the papers by O'Brien⁴ and Lohr.⁵ O'Brien has provided the theory for strong JT coupling and analyzed the dynamic effects resulting when the complex tunnels from one distortion to another, while Lohr has made a molecular-orbital calculation on the [CuCl₆]⁻⁴ complex and obtains good agreement with the experimental results reported here.

EXPERIMENTAL: EPR

Crystals of high-purity NaCl containing up to 3% high-purity CuCl were grown by the Bridgman method in sealed quartz ampoules containing a small addition of chlorine gas. This gas, introduced to prevent sticking of the crystal to the walls of the container, also converted the Cu¹ to Cu²⁺, as evidenced by the yellow-colored crystals that resulted.

Samples cleaved from the boules grown in the above manner were then heated in a nitrogen atmosphere just below the melting point for several days to reconvert the Cu²⁺ to Cu¹. The extent of reconversion was monitored by the Cu²⁺ absorption at 3500 Å and that of Cu¹ at 2800 Å.⁶

When all the Cu²⁺ was converted to Cu¹, the crystals were irradiated (x rays or Co⁶⁰ γ rays) at 77 K. EPR measurements done at this temperature without warming showed the Cu²⁺ spectrum partially obscured by that of the Cl₂⁻ center. Pulse

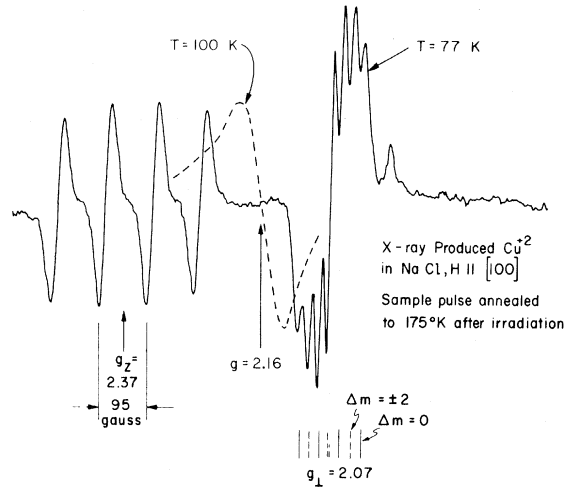


FIG. 1. EPR spectrum of Cu²⁺ in NaCl with the magnetic field parallel to one of the cube axes. This spectrum was produced by x raying the crystal at 77 K following by pulse annealing to 175 K. The solid line shows [CuCl₆]⁻⁴ complexes with distortion axes parallel to the magnetic field, as well as those perpendicular to the magnetic field. The dashed line shows the spectrum at 100 K.

warming the crystal to approximately 180 K removed the Cl₂⁻ signal with only a slight loss in intensity of the Cu²⁺ spectrum.

Since the conversion of Cu¹ to Cu²⁺ by irradiation traps a hole (removes an electron) as in the production of the Cl₂⁻ center, charge compensation is expected to occur by the formation of F centers, as evidenced by the characteristic yellow-brown color of the crystal after irradiation. In these experiments, the F-center concentration was low enough so that it was not observable by EPR.

RESULTS: EPR

At 77 K, the EPR spectrum of NaCl:Cu²⁺ with the magnetic field parallel to the [100] direction is shown in Fig. 1. The angular variation of the spectrum shows it to fit an axial spin Hamiltonian with the distortion along one of the three cubic axes and the following spin-Hamiltonian constants

$$g_{\parallel} = 2.373, \quad A/g_{\parallel} \mu_B = 95 \text{ G},$$

$$g_{\perp} = 2.070, \quad B/g_{\perp} \mu_B = 40 \text{ G},$$

$$Q'/g_{\perp} \mu_B = 20 \text{ G}.$$

The perpendicular part of the spectrum in Fig. 1 shows a complex spectrum of seven lines. Four of these come from the allowed $\Delta M = \pm 1$, $\Delta m = 0$ hyperfine transitions while the others arise from $\Delta m = \pm 2$ quadrupole induced transitions similar to what Tucker⁷ observed for Cu²⁺ in AgCl. Upon warming the crystal from 77 K, the lines in the

parallel and perpendicular parts of the spectrum are seen to broaden and disappear at $\sim 90 - 100$ K. At approximately 95 K, a single broad line starts to appear at $g = 2.16$, and both spectra, though weak, coexist at this temperature. With further heating, this line grows in intensity to approximately 10% of that of the 77 K spectrum and then disappears above 110 K. As the line first appears it is 85 G wide; it then narrows to 60 G and then broadens as it disappears. This line is shown dashed in Fig. 1. Further warming to room temperature causes the Cu^{+2} spectrum to disappear, as remeasured to 77 K.

Cooling the crystal to 4.2 K decreases the individual linewidths from ~ 25 G at 77 K to 16 G at 4.2 K. At this temperature, there appears on the parallel spectrum of the Cu^{+2} hyperfine lines a ligand hyperfine structure consisting of 13 lines. This provides evidence that the ground state is a "hole" of $(x^2 - y^2)$ symmetry with the orbital holes pointing in the direction of the four chlorines that are perpendicular to the distortion axis.^{4,8} According to O'Brien,⁴ the 13-line superhyperfine structure also indicates the ground state to be quite localized and not spread in its well. For if it were delocalized, O'Brien shows that there would result significant admixing with the $3z^2 - r^2$ state and the other two ligands would also appear in the spectrum.

The perpendicular spectrum also shows a complex ligand hyperfine structure which, because of the overlapping forbidden and allowed transitions, is too difficult to interpret simply.

STRAIN EXPERIMENT

While the experimental g values give credence to the distortion being an elongation rather than a compression,⁹ it was thought desirable to try a strain experiment for further experimental proof. Applying an axial strain along one distortion axis at low temperatures will cause a change in the ground-state energy of the three equivalent distortions and thereby a change in their relative populations. The resulting changes of signal intensity between the parallel and perpendicular components can then be interpreted in terms of a compressed or elongated octahedron. Also, as discussed below, the strain experiment allows one to measure directly the strain coefficient and make an estimate of the JT energy.^{2,3}

In these strain experiments, the $\text{NaCl}:\text{Cu}^{+1}$ crystal was sandwiched between quartz rods in the center of a cylindrical TE_{012} cavity (Ku band), the cavity itself being under zero stress. X-ray irradiation was carried out in this position at 77 K, and the aforementioned pulse-annealing procedure was then followed to eliminate the Cl_2^- center.

Then, at 77 K, dead-weight loading was applied along one of the cubic axes *perpendicular* to the magnetic field. The results of this experiment are shown in Fig. 2 for zero stress and a stress of 1100 kg/cm^2 . In Fig. 2, it can be seen that the intensity of the "parallel" part of the spectrum of the stressed crystal increased relative to the "perpendicular" part. Although Fig. 2 represents only one scan of the magnetic field for both the stressed and unstressed runs, a calculation of the change in intensity was made from a total of 20 consecutive scans with the total spectrum recorded on a signal average analyzer.

With a stress of 1100 kg/cm^2 , it was estimated from the change in intensity of the EPR spectrum that those sites distorted in the direction of the strain were reduced approximately 57% in intensity. The reason that such a change is not more readily noticeable in Fig. 2 is that the stress is applied perpendicular to the magnetic field. As a result, what is observed in Fig. 2 is an increase in the parallel spectrum by 28.5% and a net decrease in the perpendicular spectrum by 14.2%. This reduction of population of those sites distorted parallel to the strain is further proof that the octahedron is elongated rather than compressed. It should also be noted that at 77 K there appears to be no change in the g value, hyperfine splitting, or linewidth of the EPR spectrum of the stressed sample.

DISCUSSION

If it can be assumed that the Cu^{+1} is in a cubic site before irradiation at 77 K and there is no

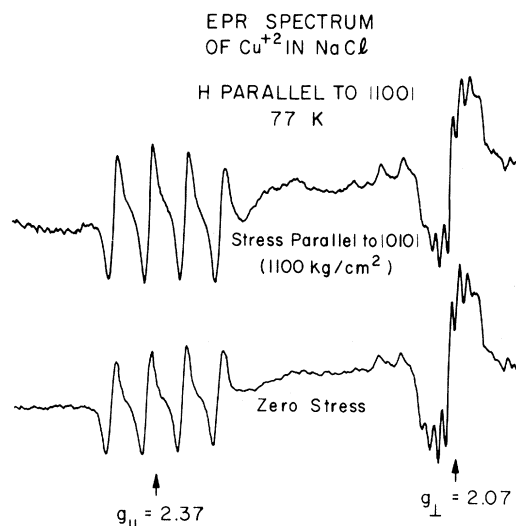


FIG. 2. EPR spectrum of Cu^{+2} in NaCl at 77 K under zero stress and stress of 1100 kg/cm^2 . The stress is applied perpendicular to the magnetic field and parallel to one of the cube axes.

significant ionic motion at this temperature, we can conclude that the crystal-field distortion that occurs when the Cu^{+2} is produced is electronic in origin, and probably is that predicted by the JT theorem. Further evidence is provided by the high-temperature spectrum which has as its g and A values $g \cong \frac{1}{3}(g_{\parallel} + 2g_{\perp})$, $A = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$, where \parallel and \perp designate the values belonging to the low-temperature spectrum. This high-temperature spectrum can be interpreted either as (a) arising from distortions which are rapidly moving among the three distortion axes, so that the measured spectrum is averaged over all positions of the rapidly moving $[\text{CuCl}_6]^{-4}$ complex, i.e., motional averaging, or (b) in terms of O'Brien's model,⁴ where the high-temperature spectrum results from populating the higher vibronic level of the complex, and the transition from an anisotropic to an isotropic spectrum depends on whether the excited states become appreciably populated before the "vibronic relaxation time" becomes large compared with $(g_{\parallel} - g_{\perp})\beta\hbar/h$. Both of these models predict the same g and A values. However, as mentioned in the section on experimental results, the coexistence of both the high- and low-temperature spectra was observed at ~ 95 K, and this can be readily explained in O'Brien's model, while the motional-averaging theory has difficulty with this point. Whether the motional-averaging model or O'Brien's model is correct could possibly be determined by a knowledge of the relaxation mechanisms.

The appearance of a static JT spectrum at low temperatures can be seen to be due to a combination of warping of the potential energy well of the ground state (see Liehr and Ballhausen¹⁰ and Öpik and Pryce,¹¹ as well as O'Brien⁴) and the effect of random strains.^{2,3} This warping in the trough of the "Mexican hat" potential may be accounted for by the inclusion of higher-order terms in the vibronic Hamiltonian with the provision that these terms reflect the symmetry of the environment, as is generally required for higher-order spin terms in the spin Hamiltonian (the linear JT term gives the axially symmetric Mexican hat potential). For sixfold coordination this "warped" potential energy surface has three minima that correspond to an axial elongation or compression of the complex, depending on the sign of the (JT) coupling. The difference in energy between the maxima and minima of the bottom of the warped potential is generally denoted by $2|\beta|$, and should the three minima correspond to an elongation of the complex in the three principal directions, then the maxima in the potential trough would correspond to a compression. The effect of random strains is to make one of the above three potential energy minima

more favorable than the other two. The importance of this effect has been noted by Ham, who concludes that for a static JT effect to be observed, the strain splitting of the energy levels must be larger than the tunneling splitting.^{2,3} For those cases in which a static JT effect has been studied, Ham has also concluded that the strain coefficient V_2 must be greater than 10^4 cm^{-1} .

For the system under consideration here, V_2 can be calculated from the stress experiment by noting the change in population (57%) for the 1100-kg/cm^2 stress at 77 K, the elastic constants¹² for bulk NaCl, and Eqs. 2.2.14 from Ref. 3,

$$\Delta E_1 = V_2[e_{zz} - \frac{1}{2}(e_{xx} + e_{yy})], \quad (2a)$$

$$\Delta E_2 = V_2[e_{xx} - \frac{1}{2}(e_{yy} + e_{zz})], \quad (2b)$$

$$\Delta E_3 = V_2[e_{yy} - \frac{1}{2}(e_{zz} + e_{xx})], \quad (2c)$$

where e_{ij} are the strain coefficients. Suppose we apply the strain along the z direction; then we wish to find the energy difference between the z and the x (or the y) direction,

$$\Delta E_1 - \Delta E_2 = kT \ln(N_1/N_2) = \frac{3}{2} V_2(e_{zz} - e_{xx}), \quad (3)$$

for which we obtain $V_2 = -1.63 \text{ eV/(unit strain)}$ ($\sim 13100 \text{ cm}^{-1}$).¹³ This value can be compared to $V_2 \sim 3 \text{ eV/(unit strain)}$ found by Sturge *et al.*¹⁴ for $\text{Al}_2\text{O}_3:\text{Ni}^{+3}$.

From our value of the strain coefficient V_2 , we can obtain an estimate of the JT energy for sixfold coordination using²

$$E_{JT} = 3V_2^2/8R^2\mu\omega^2, \quad (4)$$

where R is the nearest-neighbor distance, μ is the ligand mass, and ω is the mode vibrational frequency. If the vibrational frequency is $\sim 200 \text{ cm}^{-1}$, then we find $E_{JT} \approx 1200 \text{ cm}^{-1}$. Lohr, with his molecular-orbital (MO) treatment of the $(\text{CuCl}_6)^{-4}$ complex finds $E_{JT} = 2380 \text{ cm}^{-1}$ and vibrational frequencies of 138, 207, and 251 cm^{-1} for odd-parity vibrational modes. While only even-parity modes are responsible for the JT coupling, they should not differ greatly from those of odd parity.

The ratio $E_{JT}/\hbar\omega$ for this system is approximately 6, showing $\text{NaCl}:\text{Cu}^{+2}$ to be in the strong JT limit. In this limit, in the linear theory,^{2,3} the pq reduction factors that enter the spin Hamiltonian are diminished from unity by the strength of the JT coupling and become

$$p \rightarrow 0, \quad q \rightarrow \frac{1}{2}. \quad (5)$$

Another number important to a JT system that can be estimated from the experimental results is an estimate of $2|\beta|$, the barrier height. Lohr's⁴ MO theory shows that the transition to an isotropic spectrum at higher temperatures can

occur for a temperature of 100 K when the barrier is of the order of 300 cm^{-1} .

While measurement of V_2 for this system presents an experimental number that is of importance to JT theories, measurements of the relaxation time as a function of temperature would be very useful in providing a measure of the height of the energy barrier $2|\beta|$ and the tunneling splitting 3Γ . These experiments could be done most simply by stressing the sample at low temperatures and noting the recovery time of the EPR signal to equilibrium. One other useful measure-

ment would be to note the expected g shift of the isotropic spectrum with an applied stress.

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