PHYSICAL REVIEW B VOLUME 2, NUMBER 9 1 NOVEMBER 1970

Temperature Dependence of the Exchange Interaction in $K_2CuCl_4 \cdot 2H_2O$†

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(Received 27 May 1970)

The electron spin resonance of Cu^{2+} in $K_2CuCl_4 \cdot 2H_2O$ has been observed to change from a two-line spectrum at room temperatures to a single-line resonance at 77 °K. A detailed analysis of the Zeeman anisotropy indicates that the symmetry of the crystal field does not change with temperature. Analysis of the temperature and frequency dependence of the resonance spectrum indicates that the exchange interaction between nearest-neighbor inequivalent ions varies from J_1/k approximately 0.27 °K at 77 °K to J_1/k of the order of 0.05 °K at 300 °K. The anomalously large temperature dependence of the exchange cannot be ascribed to the effect of thermal expansion. Instead, there exists evidence that it may well be associated with the presence of a low-lying optical phonon. In contrast to the pronounced decrease of the nearest-neighbor exchange with increasing temperature, the exchange coupling between equivalent next-nearest-neighbor ions is observed either to be temperature independent or possibly to increase slightly with increasing temperature.

INTRODUCTION

The salt $K_2CuCl_4 \cdot 2H_2O$ has been investigated in the past for a variety of reasons. It is a good approximation to a body-centered-cubic Heisenberg ferromagnet undergoing a magnetic transition to the ordered state near 1 °K,[1] and it has been extensively used as a system to study the effects of exchange interactions on electron spin resonance (ESR) at high temperatures.[2] In the course of investigating the resonance properties of $K_2CuCl_4 \cdot 2H_2O$ at low temperatures, an unusual change in the ESR spectrum was observed[3,4] between room temperature and 77 °K, which has not been fully discussed in the literature.

The various measurements of the exchange interaction may be placed into three groups. At room temperature with the magnetic field along the [110] direction, the ESR spectrum consists of two lines, well resolved only at frequencies greater than 40 GHz. The lack of resolution at lower frequencies implies that the exchange is the order of 0.1 °K.[2,5] Also, at room temperature, work has been performed on the "$\frac{10}{3}$ effect" in the [001] direction. Tomita[5] infers from this type of measurement that $J/k = 0.08$ °K, while Henderson and Rogers,[6] fitting the variation in linewidth, derive 0.12 °K.[7] Lastly, there has been considerable work on the thermodynamic properties of this salt at helium temperatures. Susceptibility and specific-heat data taken around the transition temperature indicate that approximately $J/k = 0.30$ °K.[1,8] The measured low-temperature thermodynamic behavior has been analyzed in greater detail by Wood and Dalton,[9] who in a comparison with the theoretically predicted behavior of a Heisenberg ferromagnet obtained values of the exchange interaction between nearest-neighbor and next-nearest-neighbor ions to be $J_1/k = 0.28$ °K and $J_2/k = 0.056$ °K, respectively.

The present work indicates that the exchange interaction may be very strongly temperature dependent in the range from 77 °K to room temperature. Earlier reports[4,10] noting a pronounced change in the ESR spectrum in this temperature region were uncertain of its origin, but Okuda and Date[11] and the present work suggest it is the result of a temperature-dependent exchange.

EXPERIMENT

The room-temperature crystal structure of $K_2CuCl_4 \cdot 2H_2O$ has been determined from x-ray measurement[12] and neutron diffraction.[13] The overall crystal structure is tetragonal ($a = 7.45$ Å, $c = 7.88$ Å) with two molecules per unit cell, see Fig. 1(a). The Cu^{2+} ions are situated at the corner (0, 0, 0) and body center $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ of the unit cell, while the K^+ ions are located at the four sites $(\frac{1}{2}, 0, \frac{1}{4})$, $(\frac{1}{2}, 0, \frac{3}{4})$, $(0, \frac{1}{2}, \frac{1}{4})$, and $(0, \frac{1}{2}, \frac{3}{4})$. The water molecules are directly above and below the Cu ions along the c axis approximately $\frac{1}{4}$ of the unit-cell dimension, 7.88 Å, away. The Cl ions form a rhombus about the Cu in the aa plane, the axes of the rhombi of the two Cu ions within the unit cell being rotated by 90° with respect to one another, as illustrated in Fig. 1(b). It is interesting to note that the two Cu ions in the unit cell are completely equivalent except for the orientation of the rhombus of Cl ions surrounding them.

The environment of a particular Cu ion is a distorted octahedron formed by the rhombus of Cl ions in the aa plane and the water molecules above and below along the c axis. The local symmetry is orthorhombic (D_{2h}). The interatomic distances are Cu-Cl (I), 2.95 Å; Cu-Cl (II), 2.32 Å; and Cu-H_2O, 1.97 Å.

The ESR of this salt has been studied extensively by Abe *et al.*[2] They found that the resonance at high frequencies with the field in the [110] direction consisted of two lines, in accord with crystal structure.

The present work can be divided into two parts: measurements along the γ ([100]) axes and measurements along the c ([001]) axis.

The ESR in the γ direction has been measured at 35, 65, and 103 GHz between 77 °K and room temperature. Our room-temperature measurements are in good agreement with those of Abe *et al.*[2] The data indicates that the resonance of the two sites per unit cell can be described by a g tensor with principal values $g_1 = 2.35 \pm 0.01$, $g_2 = 2.12 \pm 0.01$, and $g_3 = 2.06 \pm 0.01$, where g_3 is the g value for the field parallel to the c axis, and g_1 and g_2 for the field in the two γ directions. The g_1 and g_2 axes for one ion are rotated by 90° in the *aa* plane from those of the other as predicted by the crystal structure.

The resonance at room temperature in the [110] direction discriminates between the two sites giving a two-line spectrum: one line with $g = 2.35$ and the other with $g = 2.12$. While the measurements at room temperature are as expected, the spectrum changes at lower temperatures as shown in Fig. 2. As the temperature is decreased, the two lines broaden until they overlap to form a single structureless line, which then narrows as the temperature is lowered further.

The room-temperature splitting of the lines in the γ direction increases as the microwave frequency increases, due to the difference in g values. However, at 77 °K the lines narrow to form a single resonance even at 103 GHz; the temperature at which the two lines merge decreases as the frequency increases, and the linewidth of the single line at 77 °K increases with frequency, as shown in Fig. 3. No significant change occurs in the resonances below 77 °K. The γ-axis data is summarized in Table I.

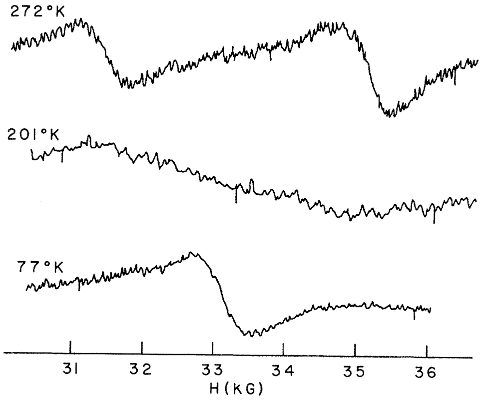
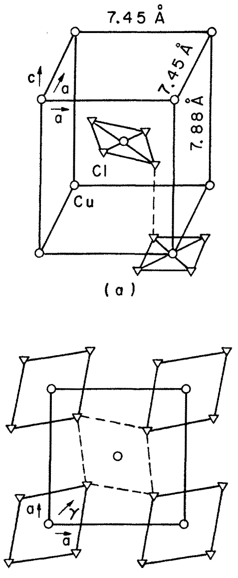


FIG. 2. Resonance spectra for $H \parallel \gamma$ at several temperatures. The frequency is 103 GHz.

In contrast to this dramatic change of the ESR spectrum along the γ axis, little variation is observed in the resonance along the c axis. With the field in this direction the two sites have the same g value and a single line is observed at all temperatures. Figure 4 illustrates the difference in line-



(a)

(b)

FIG. 1. (a) Crystal structure of $K_2CuCl_4 \cdot 2H_2O$, (b) projection on the *aa* plane. Only Cu and Cl atoms are shown.

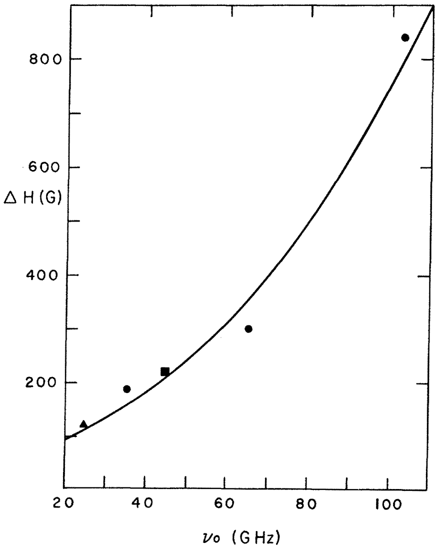


FIG. 3. Linewidth versus frequency for $H \parallel \gamma$ at 77 °K. The square is from Okuda and Date (Ref. 11), the triangle from Abe (Ref. 10), and the circles from the present work. The smooth curve is $\Delta H \propto \nu^2$.

TABLE I. Summary of the data for H ∥ γ in $K_2CuCl_4 \cdot 2H_2O$.

T(°K)	ν_0(GHz)	ΔH(G)	Type of spectrum
295	35	···	Two lines partially resolved
295	65	400	Two lines resolved
304	103	420	Two lines resolved
270	35	···	Single very broad line
245	65	···	Single very broad line
206	103	···	Single very broad line
77	35	185	Single line
77	65	300	Single line
77	103	840	Single line

width at 77° and room temperature at three different frequencies. Our room-temperature data is in good agreement with that of Henderson and Rogers.[6]

Two isomorphous salts have been investigated. One $(NH_4)_2CuCl_4 \cdot 2H_2O$ shows qualitatively very similar behavior to the potassium salt, namely, for $H \parallel \gamma$ at room temperature, two resolved resonance lines are observed which at low-temperature coalesce to a single line. No detailed quantitative study has been made of this salt. The other isomorphous crystal $(NH_4)_2CuBr_4 \cdot 2H_2O$ has been previously measured at 25 GHz by Suzuki and Watanabe,[14] who have reported $g_c = 2.04$, $g_a = g_\gamma = 2.196$ and an isotropic linewidth of 50 G at room temperature. In our measurements at 35 GHz, a single line is observed with the field along the γ axis as well as the c and a axes, at both 77 °K and room temperature. However, the linewidth is observed to be anisotropic in the aa plane, the line being broadest in the γ direction. The linewidth in each direction is narrower at 77 °K than at 300 °K. The data is summarized in Table II.

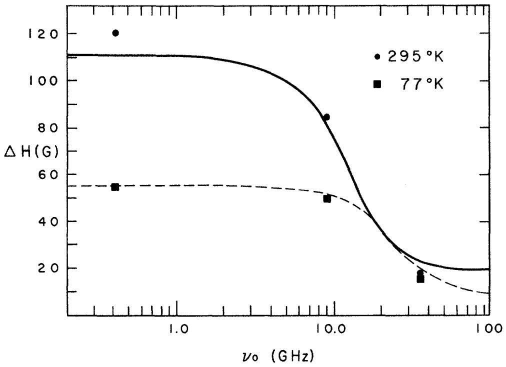


FIG. 4. The linewidth versus frequency for $H \parallel c$ at 295 and 77 °K. The smooth curves have the functional form calculated by Tomita (Ref. 5). The average exchange interaction differs by a factor of 2 between 295 and 77 °K.

DISCUSSION

Before discussing possible explanations of the observed temperature dependence of the resonance spectrum, we shall dismiss the suggestion that the phenomenon is due to the Cl group continuously changing its configuration from a rhombus at high temperature to a square array at low temperature. Quite apart from any considerations of the likelihood of such a process occuring from lattice dynamics, a detailed look at the resonance results rules it out. If at low temperature the Cl ions were to form a square, the crystal field seen by the Cu ions would have tetragonal symmetry, the fourfold axis being the crystallographic c axis. In a static field of this symmetry the g values of the two possible ground states are known.[15] For a compressed octahedron, the ground state transforms as $(3z^2 - r^2)$ and has the g values

$$g_\parallel = 2 - 3(\lambda/\Delta)^2, \qquad (1)$$

$$g_\perp = 2 - 6(\lambda/\Delta) - 6(\lambda/\Delta)^2, \qquad (2)$$

whereas for an elongated octahedron the ground state transforms as $(x^2 - y^2)$ and has the g values

$$g_\parallel = 2 - 8(\lambda/\Delta) - 7(\lambda/\Delta)^2, \qquad (3)$$

$$g_\perp = 2 - 2(\lambda/\Delta) - 4(\lambda/\Delta)^2. \qquad (4)$$

λ is the spin-orbit coupling parameter $\sim -7\times10^2$ cm^{-1} and Δ is the cubic field splitting, the order of 1.5×10^4 cm^{-1}. Since experimentally at low temperature $g_c < g_a$, the ground state in this model must be $(3z^2 - r^2)$. However, the pure $(3z^2 - r^2)$ state cannot possess a g greater than two in a static tetragonal field, whereas $g_c = 2.06$, a discrepancy too large to be ignored. The only way to explain the low-temperature g values within the model that the Cl ions form a square array is to invoke dynamic effects[16] such as zero-point motion to admix the $(x^2 - y^2)$ and $(3z^2 - r^2)$ states. Then the g values become

$$g = (1 - \alpha^2)^{1/2} g_{(3z^2 - r^2)} + \alpha g_{(x^2 - y^2)}. \qquad (5)$$

TABLE II. Summary of the data at 35 GHz in $(NH_4)_2CuBr_4 \cdot 2H_2O$.

Orientation of H	T(°K)	g value	ΔH(G)
c	295	2.05 (±0.01)	28
c	77	2.05	26
γ	295	2.19	84
γ	77	2.19	54
a	295	2.19	67
a	77	2.19	49

To account for the magnitudes of g_c and g_a, a 20% admixture is required, an amount which is an order of magnitude larger than seems likely to occur.[16] However, either to confirm or to disprove this admixture directly requires more detailed knowledge of the crystal fields than is available, as well as calculations of the lattice dynamics.

More to the point, the fact that the g values at high and low temperatures are related in the very simple way, $g_c = g_3$ and $g_a = \frac{1}{2}(g_1 + g_2)$, almost demands that the crystal fields are not changing with temperature; that is, the Cl ions must maintain a rhombic distortion about the Cu ion at all temperatures. To have the crystal fields change by virtue of the motion of the Cl ions without a change in the g value in the aa plane is extremely unlikely, especially considering that the g values at low temperature must be explained by dynamic effects in such a model.

At high temperature the g values of the resonance spectrum can be accounted for by the following model. The principal noncubic field term is considered to have tetragonal symmetry, the fourfold axis for a particular Cu ion not being the crystallographic c axis but the γ axis along which the Cl ions are farthest away from the Cu. With respect to this γ direction as the z axis, the ground state must transform as $(x^2 - y^2)$; that is, the crystal field is that of an elongated octahedron. With the reasonable value $\lambda/\Delta = -0.048$, the calculated g values are $g_\parallel = 2.35(= g_1)$, $g_\perp = 2.09(\simeq g_2 \simeq g_3)$. The deviation of g_2 and g_3 from $g_\perp$ is due to the field component of lower symmetry, which admixes the excited states into the ground level. This model implies that the crystal field produced by the water molecules along the c axis is approximately the same as that resulting from the pair of Cl ions nearer to the Cu ion. A first-principles calculation of these fields would require detailed knowledge of the bonding of the molecule.

From the discussion given above, it is necessary to conclude that the Cl ions maintain a rhombic arrangement about the Cu^{2+} at all temperatures, and that an averaging of the g values over the two inequivalent sites must occur at low temperatures to account for the single resonance with the parameters observed. Although the paramagnetic resonance spectrum of Cu^{2+} in many salts undergoes pronounced changes with temperature resulting from static and dynamic Jahn-Teller effects,[17] such a phenomenon does not appear to occur in $K_2CuCl_4 \cdot 2H_2O$. The nature of the change in the resonance, a single line at low temperature and two lines at high temperature, does not correspond to that found in any other material (except its isomorphs and perhaps $CuSO_4 \cdot 5H_2O$[3]) nor to any theoretically predicted Jahn-Teller behavior. It is, therefore, necessary to conclude that the averaging responsible for the coalescence of the two lines at low temperatures results from a strongly temperature-dependent magnetic-exchange interaction between neighboring inequivalent copper ions.

In the theory of magnetic exchange between inequivalent spins, whether or not a resolved line associated with each different site is observed depends on the relative magnitude of the exchange interaction compared to the energy difference associated with their inequivalency, in this case the difference in Zeeman energies.[18,19] For exchange energies less than approximately

$$J_1 \simeq \tfrac{1}{2}(g_1 - g_2)\,\beta H, \tag{6}$$

two resonances are observed, whereas for larger exchange energies only a single-resonance line occurs. Experimentally, the temperature at which the transition from two resolved lines to a single line takes place is found to decrease with increasing frequency and field. To explain quantitatively the measured change in the resonance for $H \parallel \gamma$, the exchange interaction must be a factor of 5 larger at 77 °K than at room temperature.

The linewidth of the single exchange narrowed line at 77 °K is shown in Fig. 3 as a function of frequency for $H \parallel \gamma$. In general, the linewidth is the result of the combined influence of the dipolar, hyperfine, and exchange interactions and the difference in Zeeman energies. At low frequencies the dipolar and hyperfine interactions are larger than the Zeeman energy difference, and, in addition, the exchange is comparable to $g\beta H$, so that the "$\frac{10}{3}$ effect" must be considered. Because of both the uncertainties in the theory of this effect and the inaccuracies in data, no detailed comparison between theory and experiment has been attempted at low frequencies. At high frequencies the width of the resonance line is primarily the result of the inequivalence of the g values and the exchange narrowing. In this limit the linewidth[19] is given by the expression

$$(g_{av}\,\beta)\,\Delta H \approx [(g_1 - g_2)\beta H]^2/8J_1 \quad . \tag{7}$$

Using the measured high-frequency linewidth and Eq. (7), the exchange interaction between nearest-neighbor inequivalent ions is calculated to be $J_1/k = 0.3$ °K. This value is in good agreement with the result obtained by Wood and Dalton[9] who used the low-temperature thermodynamic properties of $K_2CuCl_4 \cdot 2H_2O$ to estimate the nearest-neighbor exchange coupling to be 0.28 °K. It may be, however, that this agreement is in part fortuitous since Gulley *et al.*[20] have found systematic discrepancies between theory and experiment in exchange narrowing. For example, in $KMnF_3$ they found that $\Delta H^{\text{theor}}/\Delta H^{\text{expt}} = 2.8$, a discrepancy which they ascribe to the fact that the spin autocorrelation functions in that material cannot be characterized by a single decay constant.

From measurements over a wide range of frequencies, i.e., from 9 to 103 GHz, it is possible to estimate the temperature dependence of the exchange between nearest-neighbor inequivalent sites. Although the exact numerical relationship between the exchange and the line shape may not be known precisely, the *dependence* of the line shape on the exchange is assumed to be that predicted theoretically. Then, from the temperature variation of the linewidth of the single line observed at low temperatures, the exchange interaction J_1 is found to vary as illustrated in Fig. 5. The exchange has been taken to be 0.27 °K at 77 °K to agree with the low-temperature thermodynamic measurements.[1,8] The other low-temperature points in Fig. 5 are then determined in relation to this value at 77 °K. At a given frequency and field the temperature at which the two lines coalesce may be used with Eq. (6) to determine J_1. The exchange determined in this manner by Okuda and Date[11] is indicated in Fig. 5. This procedure is subject to some uncertainty in that theoretically the condition for the resolution of two distinct lines is only semiquantitative.

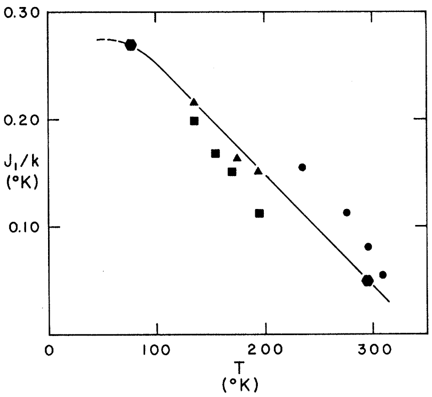


FIG. 5. Nearest-neighbor exchange J_1 versus temperature. The triangles and squares are from linewidth data at 35 and 65 GHz, respectively, and are normalized such that J_1/k at 77 °K is 0.27 °K. The circles are from the coalescence data of Okuda and Date (Ref. 11). Analysis of the linewidth at room temperature and of the change in the spectrum with frequency (see text) suggests that J_1/k at 295 °K is 0.05 °K. All the data are consistent within the experimental error.

The room-temperature linewidth of the resolved lines for $H \parallel \gamma$ is about 400 G, much greater than the linewidth for $H \parallel c$. Since exchange between unlike spins contributes to the second moment and hence the linewidth, the large difference between the measured linewidth for $H \parallel \gamma$ and that for $H \parallel c$ (where all the spins are alike) indicates that the exchange between nearest neighbors J_1 is appreciable at room temperature. Quantitative second-moment calculations and the measured second moment give $J_1/k \approx 0.05$ °K, supporting the above conclusion. Thus, from the frequency dependence of the $H \parallel \gamma$ data and considerations of the resolved linewidth, the room-temperature value of J_1/k is fixed at 0.05°. This is shown in Fig. 5.

The problem now is to explain the different temperature variation in the resonance absorption for the magnetic field parallel to the *c* axis, an orientation in which the *g* values of the two sites are equal. The linewidth with the field in this direction is the result of the combined effect of the dipolar, hyperfine, and exchange interactions. Cu^{2+} in an elongated octahedral environment in a dilute salt is found to have a hyperfine coupling of about 10^{-2} cm^{-1}.[21] Taking this value for $K_2CuCl_4 \cdot 2H_2O$ and comparing it to the dipolar coupling as determined from a second-moment calculation shows that the contributions are nearly equal in this salt. The exchange may be estimated using an equation similar to (7), where the broadening in this case is due to the dipolar and hyperfine interactions instead of a difference in *g* values. Using theoretical estimates of the dipolar and hyperfine broadening and the measured exchange narrowed linewidth, the exchange is calculated to be roughly 0.1 °K. This calculated value is a combination of J_1 and J_2, a combination which depends upon the number of neighbors associated with each species of exchange. The frequency dependence of the linewidth, illustrated in Fig. 4, is a result of the "$\frac{10}{3}$ effect," which can be used to deduce an exchange interaction.[5,6] Outside the region where it is a function of frequency, the linewidth, and hence the exchange, is observed to vary only by a factor of 2 between 77 and 300 °K. Thus, the result for $\vec{H} \parallel c$, is in marked contrast to the result for $\vec{H} \parallel \gamma$.

The reason for the pronounced difference in temperature dependence of the resonance lines in the two orientations is that the characteristics of the absorption are determined by different parameters. (Anisotropy of the exchange is not expected to have a significant effect since the ratio of anisotropic to isotropic contributions is the order of $\Delta g/g$ in insulators.[22]) For $H \parallel c$, the Zeeman energy of all spins is the same so that exchange between nearest-neighbor and next-nearest-neighbor spins contributes to the exchange narrowing of the dipole and hyperfine broadened line. However, for $H \parallel \gamma$ only the exchange between nearest-neighbor inequivalent sites is responsible for the coalescence of the two resonance lines resulting from the difference in Zeeman energies, and for the linewidth at low temperatures when only one line is observed. At high temperatures where the two lines are resolved, an exchange between nearest-neighbor inequivalent sites broadens the lines whereas exchange between next-nearest-neighbor equivalent sites narrows the individual lines separately.

To do more than present a qualitative argument for the difference in resonance behavior in the two orientations is difficult in the absence of a quantitative theory. However, taking the Wood-Dalton[9] values for the nearest- and next-nearest-neighbor exchange interactions to be $J_1/k = 0.28\,^\circ\mathrm{K}$ and $J_2/k = 0.06\,^\circ\mathrm{K}$ at low temperature, it is difficult to see how J_1/k could drop to $0.05\,^\circ\mathrm{K}$ at room temperature and have the linewidth for $H \parallel c$ only increase by a factor of 2 without an increase in J_2 with increasing temperature to compensate partly for the large change in J_1.

Although the speculation that J_2 may increase with increasing temperature is perhaps unwarranted by the experimental data, it is clear that the measurements rule out the possibility that J_2 can be varying with temperature in the same manner as J_1. If this were true the linewidth for $H \parallel c$ would have to change by much more than the factor of 2 experimentally observed.

Philp and Adams[23] have determined the pressure dependence of the Curie temperature of $K_2CuCl_4 \cdot 2H_2O$ to be

$$\left(\frac{\partial T_c}{\partial p}\right)_T = -1.5\times10^{-11}\,^\circ\mathrm{K\,cm^2/dyn} \ . \tag{8}$$

If the exchange constant and the ordering temperature are proportional to one another, the change in J between room temperature and $77\,^\circ\mathrm{K}$ due to thermal expansion can be estimated from the relationship

$$\frac{1}{J}\left(\frac{\partial J}{\partial T}\right)_P = \frac{\beta}{K}\,\frac{1}{T_c}\left(\frac{\partial T_c}{\partial P}\right)_T \ . \tag{9}$$

Taking the thermal expansion coefficient β to be[11] $9\times10^{-5}\,^\circ\mathrm{K}^{-1}$ and the isothermal compressibility K to be 4×10^{-12} cm^2/dyn, the calculated variation in J between 77 and 300 °K is only 6%, a factor at least 50 smaller than the measured change of J_1. Clearly, the effects of the bulk thermal expansion of the crystal are not sufficient to account for the temperature dependence of the exchange or the difference between the dependence of J_1 and J_2.

Recently, Choh and Stager[24] have studied the NMR of chlorine in $K_2CuCl_4 \cdot 2H_2O$ and have determined the quadrupole coupling constants for the different sites. Of particular interest to the present discussion is the result that the quadrupole interaction for one site is very strongly temperature dependent, decreasing with increasing temperature by approximately 6% from 0 to 300 °K. (The quadrupole interaction of the other site shows no such anomalous temperature dependence.) The preliminary NMR results demonstrate the existence in this salt of a very low-lying optical phonon mode, which gives rise to a change of the electric field gradient at one of the Cl sites because of the ionic motion associated with thermal population of the mode at high temperatures. This mode may be a rotational (librational) mode of the copper complex as has been observed by chlorine resonance in other systems,[25,26] but in $K_2CuCl_4 \cdot 2H_2O$ further experimental work and theoretical analysis are needed before the mode responsible for temperature dependence can be definitely identified. Nevertheless, the NMR does indicate that the electric field gradient and hence the mean-square displacement of the chlorine ion are strongly temperature dependent.

The motion of chlorine ions as observed by NMR is of importance to these measurements in that the Cl ions are undoubtedly involved in the superexchange interaction between nearest-neighbor copper ions. The crystal structure of $K_2CuCl_4 \cdot 2H_2O$ is such that the overlap of wave functions responsible for the magnetic exchange is most likely via the path Cu-Cl-H_2O-Cu. Since the exchange must involve the Cl ion, the temperature dependence of the exchange appears to be associated with the existence and thermal population of the optical mode.

The fact that an optical mode is responsible for the strong temperature dependence of the exchange is consistent with several other features of the results. On the basis of this mechanism one would expect the temperature dependence of the exchange not to be related in a simple way to the pressure dependence, and thus Eq. (8) to be an inappropriate description of the present phenomenon as is observed experimentally. In addition, the difference in the temperature dependence of J_1 and J_2 is not surprising. The $CuCl_4 \cdot 2H_2O$ complex possesses low symmetry, and the motion associated with the optical mode is likely to be highly directional in nature. These features, coupled with the fact that the paths for the exchange between nearest neighbors and next nearest neighbors are completely different, can account for the drastically dissimilar temperature behavior of J_1 and J_2 required to explain the ESR data.

The measurements made on isomorphous salts are not inconsistent with these arguments. The replacement of the cation K by (NH_4) or Rb makes little difference on the magnitude of the temperature dependence of the exchange presumably because the cation does not affect the modes of the copper complex. Similarly, deuteration has no appreciable influence on the magnetic properties.[11] However, the bromine salts possess considerably larger exchange interactions between inequivalent nearest neighbors, and as the data in Table II show, the temperature dependence of J in $(NH_4)_2CuBr_4 \cdot 2H_2O$ is much smaller than in the Cl salts. This difference in temperature dependence must result from a marked alteration of the modes of the copper octahedral complex by the substitution within it of Br for Cl.

[†] Work supported in part by the National Science Foundation and by the Advanced Research Projects Agency.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 9 1 NOVEMBER 1970

Inelastic Neutron Scattering from Single-Domain $\mathrm{BaTiO_3}$[†]

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(Received 4 May 1970)

The lattice dynamics of tetragonal $\mathrm{BaTiO_3}$ have been investigated by inelastic neutron scattering from a single-domain crystal. Measurements were carried out on two projections, ($hk0$) and ($h0l$); the study revealed extreme anisotropy in energy and damping of the soft optic mode, depending upon the polarization vector $\vec{e}$. The lowest transverse optic branch with the wave vector $\vec{q} \parallel [110]$ and $\vec{e} \parallel [1\bar{1}0]$ shows well-defined phonons except for small q values (< 0.05 Å^{-1}), where they become overdamped. The soft-mode energy increases rapidly with q and extrapolates back to 4.5 meV at the zone center, in agreement with the previous Raman measurements. On the other hand, the soft modes with $\vec{e} \parallel [100]$ (with $\vec{q} \parallel [010]$ or $[001]$) have unusually low energies and high damping constants for the entire zone. They cross over the acoustic branches, resulting in marked anomalies for the latter. The present study establishes the validity of the soft-mode model for ferroelectricity in $\mathrm{BaTiO_3}$, as was the case for $\mathrm{SrTiO_3}$. The important feature for $\mathrm{BaTiO_3}$ is the greatly enhanced polarization correlation along the [100] direction compared with other perovskites.

I. INTRODUCTION

Barium titanate has long been considered as the prototype of displacive ferroelectrics. It crystallizes in a simple perovskite structure, and its properties through the Curie temperature at 130 °C have been thoroughly investigated. There is, however, one important characteristic of this ferroelectric yet to be clarified, namely, the lattice dynamical aspect of the transition in terms of the soft optic mode.