distributions. Also, the three-electron process listed as process E in Table I would produce much faster electrons than are observed.

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Direct Measurement of an Order Parameter Associated with the 110.9-K Displacive Phase Transition in K_2ReCl_6†

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The temperature dependence of an order parameter associated with the 110.9-K displacive phase transition in K_2ReCl_6 is measured directly in the tetragonal phase using rotation patterns obtained from nuclear Zeeman quadrupole resonance studies on single crystals. The measurements extend over the temperature range $103 < T < 110.9$ K. The order parameter follows a Landau-like behavior to within 0.4 K of the transition temperature. The zero-temperature coherence length is calculated to be 9.2 Å, which is approximately the distance between adjacent $ReCl_6$ octahedra. Critical fluctuations in K_2ReCl_6 are therefore of short range.

I. INTRODUCTION

Several years ago O'Leary and Wheeler[1] published the results of a comprehensive study of the displacive phase transition occurring at 110.9 K in the antifluorite-type crystal K_2ReCl_6. X-ray diffraction, Raman scattering, infrared absorption, and pure nuclear quadrupole resonance measurements all indicate that the phase transition involves a structural alteration which reduces the symmetry from cubic to tetragonal and that the phase transition is of the second order in the Landau sense.

Above 110.9 K each $ReCl_6$ octahedron occupies the center of a cubic cage defined by K ions. The principal axes of the octahedra are parallel to the cubic axes. Below 110.9 K the crystal suffers a tetragonal distortion parallel to one of the cubic axes; this distortion is accompanied by a small ferro rotation of the $ReCl_6$ octahedra about the distortion axis. The crystals are usually multiple domained in the low symmetry phase. In a particular domain the distortion axis may be parallel to any one of the cubic axes of the high symmetry phase. Therefore there are $ReCl_6$ octahedra rotated about each of these cubic axes. The rotation angle for the octahedra constitutes an order parameter for the phase transition and therefore its measurement is of inherent interest. O'Leary and Wheeler attempted to ascertain the chlorine positions in the tetragonal phase by x-ray diffraction but owing to the multiple domain structure of the crystals were only able to estimate a maximum angle of rotation of about 2°.

In this paper we will describe an experiment capable of providing a direct measurement of the rotation angle of the $ReCl_6$ octahedra in the tetragonal phase of K_2ReCl_6 and present the results obtained over the temperature range 103–110.9 K. A second phase transition to a structure of still lower symmetry occurs at ~103 K.

II. TECHNIQUE OF MEASUREMENT

The chlorine nuclei in K_2ReCl_6 have spin $I=\frac{3}{2}$ and site symmetry C_{4v} above T_c (110.9 K) with the axes of symmetry along the Re-Cl bonds. The Hamiltonian describing the nuclear quadrupole interaction at a chlorine nucleus may be written

$$\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)}\left[3I_z^2 - I(I+1)\right], \qquad (1)$$

where eq is the component of the electric field gradient (efg) along the Re-Cl bond (z axis) and eQ is the scalar quadrupole moment of the chlorine nucleus. The result of $\mathcal{H}_Q$ operating on the nuclear spin states is to produce a pair of doubly degenerate nuclear spin levels $|\pm\frac{3}{2}\rangle$ and $|\pm\frac{1}{2}\rangle$ separated in energy by $\frac{1}{2}e^2qQ$. The observation of magnetic dipole transitions between these states corresponds to a pure nuclear quadrupole resonance (NQR) experiment of the type reported by O'Leary and Wheeler.[1]

It a static external magnetic field $\vec{H}$ is applied to the sample the Cl nuclei also experience a Zeeman interaction as described by the Hamiltonian

$$\mathcal{H}_M = -\gamma\hbar\vec{I}\cdot\vec{H}, \qquad (2)$$

where γ is the chlorine magnetogyric ratio. The effect of $\mathcal{H}_M$ is to lift the degeneracy of the $|\pm\frac{3}{2}\rangle$ and $|\pm\frac{1}{2}\rangle$ nuclear spin states. The transition frequencies between these Zeeman split states are given by

$$\nu = (e^2qQ/2h) \pm (\gamma H/2\pi)(3-f)\cos\theta, \qquad (3)$$

where $f=[1+4\tan^2\theta]^{1/2}$ with θ the angle between $\vec{H}$ and the Re-Cl bond axis. The (+) sign in Eq. (3) corresponds to the transition $|-\frac{3}{2}\rangle \to |-\frac{1}{2}\rangle$ and the (−) sign to the transition $|+\frac{3}{2}\rangle \to |+\frac{1}{2}\rangle$.

Below T_c the site symmetry at the chlorine nuclei is no longer strictly C_{4v} and the quadrupole interaction is no longer axially symmetric. However, more than 90% of the efg at a chlorine site arises from the charge distribution within the host $ReCl_6$ complex and less than 10% from the neighboring ions.[2] Therefore, it is reasonable to assume that Eq. (3) is also valid in the tetragonal phase and that $\theta=0$ corresponds to the case that the magnetic field is aligned parallel to the Re-Cl bond.

The observation of the nuclear spin transitions given by Eq. (3) as a function of the magnetic field direction provides an accurate method of locating the principal axes of the efg, that is, the orientations of the Re-Cl bonds.

In the cubic phase the crystal is aligned to make θ equal to zero. In the tetragonal phase the equilibrium positions of the $ReCl_6$ octahedra rotate about the axes of distortion. The amount of rotation at any temperature can be measured by rotating the crystal about the distortion axis so as to obtain again the $\theta=0$ condition. That is, the temperature dependence of this order parameter in the tetragonal phase of K_2ReCl_6 can be measured directly using rotation patterns obtained from the nuclear Zeeman quadrupole resonance method applied to the study of a single crystal.

III. EXPERIMENTAL MEASUREMENTS

A powder sample of K_2ReCl_6 was purchased from Johnson, Matthey, and Mallory. Single crystals were grown by slow evaporation from slightly acidic (pH = 3) aqueous solutions. The crystal used for the experiments was mounted so that it could be rotated about two perpendicular axes in the magnetic field. Therefore, the crystal could be aligned about the [010] and [001] axes each to an accuracy of $\pm\frac{1}{5}$° (the magnetic field is taken along the [100] direction). The temperature of the crystal was maintained using a conventional gas-flow system and was held stable to within ±0.1 K. Two calibrated copper-constantan thermocouples positioned above and below the crystal differed by at most 0.2 K and usually much less. The value of T_c obtained was 110.9 ± 0.2 K in good agreement with the value measured by O'Leary and Wheeler.[1]

A Varian Associates wide-line spectrometer with a 12-in. electromagnet was used for the experiments. Because of the cross-coils probe arrangement, the intensity of the resonance lines depends on the orientation of the principal axes of the efg with respect to the transmitter coil. The intensity of the resonance for a particular chlorine

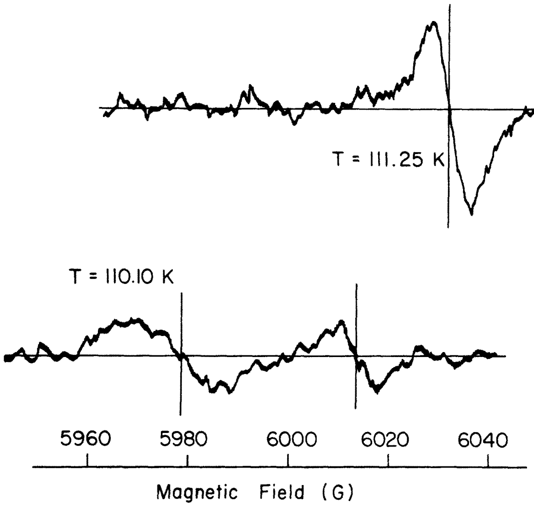

FIG. 1. Recorder traces of ^{35}Cl resonance signal above and below T_c at a frequency of 16.363 MHz.

nucleus is a maximum when the axis of the transmitter coil is in the plane perpendicular to the Re-Cl bond for that nucleus. The intensity decreases as the crystal is rotated. As a result, only those chlorine nuclei with their Re-Cl bonds along the magnetic field direction were observed.

Above T_c, the ^{35}Cl resonance line having the frequency as given by Eq. (3) with the (+) sign was observed using an applied magnetic field of approximately 6 kG. The frequency was kept fixed and the magnetic field varied to obtain the resonance. A typical recorder trace of the ^{35}Cl resonance signal is shown in Fig. 1 for a temperature of 111.25 K. As the crystal was rotated about the [010] and [001] directions the position of the center of the resonance line traced out curves whose shapes matched the $(3-f)\cos\theta$ angular dependence predicted by Eq. (3). The minima of these two curves established the position of the crystal when the magnetic field was aligned along an Re-Cl bond.

Below T_c, the single line was replaced by two lines as shown in Fig. 1 for a temperature of 110.10 K. A small rotation of the crystal (~1°) in either a clockwise or counterclockwise sense about the [001] direction caused the upper field line to move a few gauss further upfield and the lower field line to split. The upper field line may therefore be identified with those ^{35}Cl nuclei that still have their Re-Cl bonds along the magnetic field direction; the lower field line with ^{35}Cl nuclei associated with Re-Cl bonds that have rotated by angles of $\pm\phi$ away from their high-temperature equilibrium positions in the (001) plane. Since there are twice as many nuclei contributing to the lower field line one might expect this line to have twice the intensity of the upper field line. However, since the rotation angle is only of the order of a few degrees, a small error in the alignment of the crystal above T_c would imply that not all of the rotated Re-Cl bonds would make angles of $\pm\phi$ to the direction of the magnetic field, but rather would be distributed over ranges of angles $\pm(\phi\pm\delta\phi)$, where $\delta\phi$ is the original error in alignment of $\sim\frac{1}{5}°$. As a result the lower field line would be broadened. On the other hand, there should be no additional broadening of the upper field line from that observed in the cubic phase. Figure 1 verifies this argument since the upper field line below T_c exhibits the same linewidth as the single line above T_c, whereas the lower field line below T_c has approximately three times this width.

The variation of the positions of the resonance lines in the tetragonal phase is measured as a function of the angle of rotation of the crystal about the axis of distortion (the [100] axis for the ^{35}Cl nuclei observed). A typical set of data is shown in Fig. 2 for the sample at a temperature of 106.2 K. Both of the lines exhibit the functional dependence on the angle of rotation θ as predicted by Eq. (3). In fact, the dashed lines represent least-squares fits of the data to that functional dependence. The position of the minimum of the curve fitted to the lower field line gives the position of the Re-Cl bond axis in the tetragonal phase relative to its position in the cubic phase. We see from Fig. 2 that at 106.2 K the rotation angle $\overline{\phi}$ of the ReCl$_6$ octahedra and therefore the value of this order parameter is ~3.1°.

Figure 3 shows the temperature variation of the rotation angle for $103 < T < 110.9$ K. The angle $\overline{\phi}$

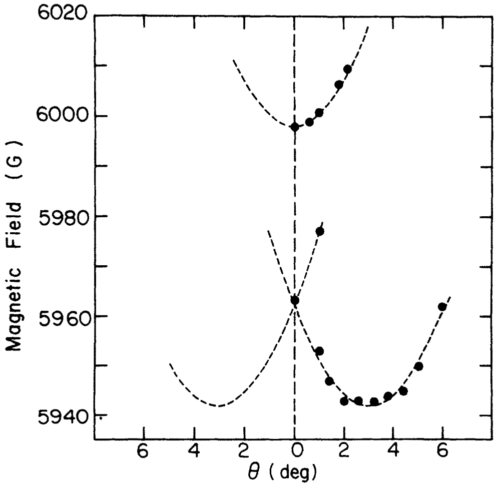

FIG. 2. Resonance line positions vs the angle of rotation of the crystal is shown for a temperature of 106.2 K. The value $\theta = 0$ corresponds to the symmetry position above T_c. The dashed lines are least-squares fits to the data.

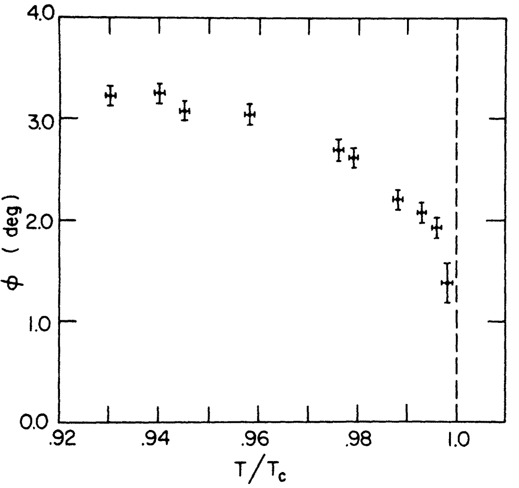

FIG. 3. A plot of the rotation angle $\bar{\phi}$ vs T/T_c for K_2ReCl_6. The dashed line indicates the phase transition.

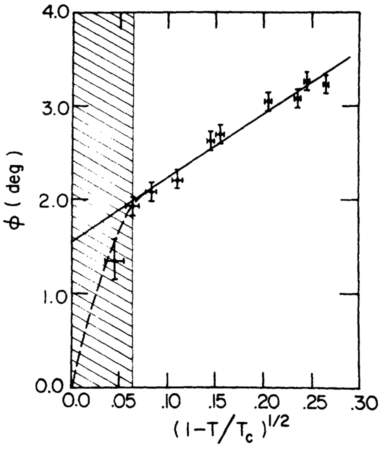

FIG. 4. A plot of $(1-T/T_c)^{1/2}$ vs $\bar{\phi}$ for K_2ReCl_6. The solid straight line is a least-squares fit to the upper nine data points. The dashed line indicates a possible variation of $\bar{\phi}$ in the critical (shaded) region.

is plotted as a function of T/T_c. The graph shows the manner in which the order parameter increases as T is decreased below T_c.

IV. DISCUSSION OF RESULTS

Figure 4 shows a plot of the rotation angle $\bar{\phi}$ as a function of $h(1-T/T_c)^{1/2}$. Except for the single data point closest to T_c the data can be represented by the straight line shown. That is, the order parameter associated with the 110.9-K phase transition in K_2ReCl_6 follows a Landau-like behavior,[3] at least for values of $(1-T/T_c)^{1/2} \geq 0.063$, or to within 0.4 K of the actual transition temperature.

Since all of the available evidence indicates that the phase transition is of second order, one might expect that $\bar{\phi}$ will decrease continuously to zero as T approaches T_c. If this is to occur then $\bar{\phi}$ must deviate from the $T^{1/2}$ dependence near T_c. The data point taken closest to T_c is consistent with this hypothesis; the dashed line may indicate the behavior of $\bar{\phi}$ close to T_c. The shaded region in Fig. 4 would then correspond to the critical region. From a knowledge of the temperature range ΔT of the critical region, an estimate of the zero-temperature coherence length λ can be deduced from the expression[4]

$$\lambda = (k_B/\Delta C)^{1/3}(T_c/\Delta T)^{1/6}/2\pi^{1/3}, \tag{4}$$

where ΔC is the change in the specific heat per unit volume for the temperature change ΔT, and k_B is the Boltzmann constant. Using the data of Busey *et al.*[5] for ΔC and setting $\Delta T = 0.4$ K in Eq. (4) yields $\lambda \simeq 9.2$ Å, which is of the same order of magnitude as the distance between adjacent $ReCl_6$ octahedra. This result indicates that the critical fluctuations in K_2ReCl_6 are of short range.

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