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SOFT ROTARY MODE AND STRUCTURAL PHASE TRANSITIONS IN K_2ReCl_6

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The triple-axis neutron scattering technique has been used to observe the soft-phonon modes associated with the second-order structural phase transitions in the cubic antifluorite K_2ReCl_6. The transverse $(ReCl_6)^{-2}$ rotary mode has been found to be soft all along the [ζ00] direction, with the structural distortions being triggered by a condensation first at the zone center and then at the [100] zone boundary. In addition to the soft phonon modes there is a temperature dependent central component to the spectrum along the [ζ00] direction.

Materials of the cubic antifluorite class (R_2MCl_6) have received increased interest recently since many of them exhibit magnetic and/or structural phase transitions at low temperatures. The potassium hexachlorometallates (K_2MCl_6) of the 5d series, for example, generally undergo a series of transitions with decreasing temperature. These transitions systematically occur at successively lower temperatures as the 5d series[1] is traversed from W to Pt, and in fact K_2PtCl_6 remains cubic down to the lowest temperatures.

The most extensively studied compound of this group is K_2ReCl_6, for which transitions at 111, 103, 76 and 12 K have been observed.[2] The transitions at 76 and 12 K are first order in nature, with the 12 K transformation being associated with antiferromagnetic order.[3] Our principal interest here, however, concerns the second-order structural transitions occurring at 111 and 103 K, which are displacive in nature and may be expected to be driven by a soft phonon mode. This expectation arises from the comprehensive work of O'Leary and Wheeler.[4] They concluded on the basis of crystallographic, spectroscopic, and thermodynamic measurements that these transitions in K_2ReCl_6 are driven by an optical phonon branch associated with the rotation of the $ReCl_6$ complex. An interesting feature of these transitions is that they are predicted to be triggered by the same phonon branch, which first condenses at the zone center (Γ point) at 111 K and then at the [100] zone boundary (X point) at 103 K. Since this mode is not Raman or infrared active in the cubic phase, however, no direct confirmation could be made. Further evidence of a soft rotary mode in the high temperature phase has been obtained by Van Driel, et al,[5] using Cl^{35} nuclear quadrupole resonance. Based on the lattice-dynamics model of O'Leary and Wheeler, they predicted that the zone-center rotary mode softens from 5.7 meV (46 cm^{-1}) at room temperature to 1.9 meV just above the 111 K phase transition. The present neutron scattering studies have revealed that the transverse rotary mode is in fact soft all along the [ζ00] direction, and condenses first at Γ and then at X in agreement with the work of O'Leary and Wheeler.[4] Furthermore, in addition to the soft phonon scattering we find a temperature dependent central component (central peak) to the spectrum for wavevectors along the [ζ00] direction.

In the antifluorite structure the Re ions occupy a face-centered cubic lattice and are each surrounded octahedrally by Cl ions located a distance ±u (unspecified by symmetry) along the six equivalent cubic axes. The K ions are arranged in an eight-fold cubic coordination around each Re in positions such as $\pm\frac{1}{4}\pm\frac{1}{4}\pm\frac{1}{4}$. Each K ion is shared between four Re ions, but the octahedral complexes are not shared and may rotate independently. This contrasts with the situation found in the cubic perovskite (RMX_3) structure in which many of the displacive phase transitions[6] are associated with rotations of the X_6 octahedra but these octahedra are joined together.

For the purposes of the low energy phonon excitations in which we are presently interested the $ReCl_6$ complex may be considered as a single unit with translational and rotational degrees of freedom. For phonons propagating along the [ζ00] direction the rotational motions decompose into two irreducible representations corresponding to rotations of the octahedra about one of the principal axes. In one case the axis of rotation is perpendicular to the phonon wavevector $\vec{q}$, so that the displacement of two of the Cl ions is perpendicular to $\vec{q}$ while the displacement of the other two is par-

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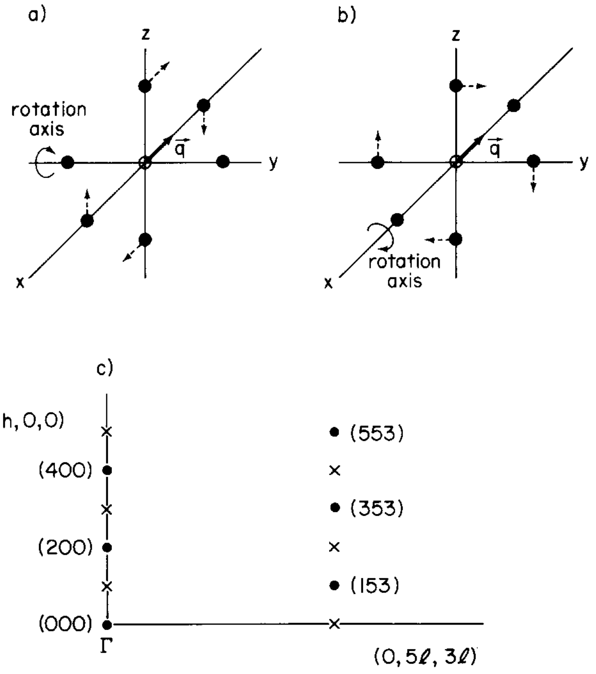

Fig. 1. Displacements of the Cl ions (solid circles), which surround octahedrally the Re ion (open circle) at the origin, for a) the "mixed" or longitudinal rotary phonon mode; b) the transverse rotary mode, which is the soft mode in the system; c) the scattering plane in reciprocal space in which the measurements of the transverse rotary mode we made. The solid circles denote the reciprocal lattice points belonging to the high temperature fcc phase, and the X's indicate the positions of the zone boundaries in the [ζ00] direction.

allel to $\vec{q}$, as shown in Fig. 1a. The atomic displacements are therefore neither transverse nor longitudinal to the phonon propagation direction. The other type of rotational motion corresponds to the axis of rotation parallel to $\vec{q}$ as shown in Fig. 1b. Since the displacements are purely transverse to the phonon propagation direction we refer to this as the transverse rotary mode.[7] This is the mode that is involved in the displacive transitions. The condensation at the zone center (Γ) corresponds to a uniform rotation of the Cl_6 octahedra about one of the cubic axes (with three possible types of domains). The condensation at the [100] zone boundary (X) point means that the octahedra in the planes perpendicular to the [100] direction rotate together, but that alternate planes rotate in the opposite sense, doubling the unit cell in the [100] direction.

The neutron scattering measurements were carried out on triple-axis neutron spectrometers at the Brookhaven High Flux Beam Reactor. Pyrolytic graphite (002) crystals were used for the monochromator and analyzer. The incident energy was chosen to be 13.5 meV so that a pyrolytic graphite filter could be used to suppress higher order wavelength contaminations in the incident beam. The sample weighed .55 gm.

The neutron cross section for creation of a phonon is given by

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k'}{k}\,\frac{n_\lambda(\omega)+1}{\omega_\lambda(\vec{q})}\,|F(\vec{K})|^2 \qquad (1)$$

where k and k' are the incident and final wavevectors of the neutron, $\hbar\vec{K}$ is the change in momentum of the crystal, $\hbar\omega_\lambda(\vec{q})$ is the energy of the λth phonon mode of wavevector $\vec{q}$, and $n_\lambda(\omega)$ is the phonon thermal population factor. For phonon destruction $n_\lambda(\omega) + 1$ is replaced by $n_\lambda(\omega)$. The intensity of the phonon scattering is controlled by the phonon structure factor

$$F(\vec{K}) = \sum_j \frac{b_j e^{-W_j(\vec{K})}}{(M_j)^{\frac{1}{2}}}\,[\vec{K}\cdot\hat{e}_j(\lambda,\vec{q})]\,e^{i\vec{K}\cdot\vec{r}_j} \qquad (2)$$

where $\vec{r}_j$ is the position of the jth atom of mass M_j and nuclear scattering amplitude b_j, $\exp(-W_j(\vec{K}))$ is the Debye-Waller factor, $\hat{e}_j(\lambda,\vec{q})$ is the eigenvector for the jth atom for phonon branch λ of wavevector $\vec{q}$, and the sum is over all atoms in the (primitive) unit cell. The Cl_6 rotary mode involves only displacements of the Cl ions, which are located on the cubic axes a distance u away from the origin (or equivalent fcc positions) with u unspecified by symmetry. For the transverse rotary mode in the [ζ00] direction, with the displacements as shown in Fig. 1b, we then have

$$F(\vec{K}) = \frac{b_{Cl}\, e^{-W_{Cl}}}{(M_{Cl})^{\frac{1}{2}}} \left(\frac{2\pi}{a}\right) 2i\,[k\sin 2\pi u\ell - \ell\sin 2\pi uk]. \qquad (3)$$

For crystals with cubic symmetry it is generally convenient to make measurements in high-symmetry scattering planes such as (hk0) or (hkk), in which both longitudinal and transverse modes in the principal symmetry directions are usually accessible to measurement. For the soft phonon in which we are primarily interested for the present case, however, we see that $F(\vec{K})$ vanishes identically if k = ℓ, or either k or ℓ is zero. Thus in order to observe this mode it is necessary to orient the crystal into a lower symmetry scattering plane such as shown in Fig. 1c. Here the solid circles denote the reciprocal lattice points in the high temperature (cubic) phase, and the X's denote the superlattice peaks which are associated with the transition at 103 K. These positions are zone boundary points in the fcc phase. We remark that the rather unusual behavior of the structure factor for the transverse rotary mode allows a unique identification of this mode as the soft phonon.

The scattering observed at $\vec{Q}$ = (3, 5, 3) is shown in Fig. 2a at a temperature of 200 K. The peaks at ±1.8 meV are the rotary phonon observed in neutron energy gain (E < 0) and energy loss (E > 0), and the intense scattering at E = 0 is the Bragg peak. At 150 K (Fig. 2b), the energy of the (zone center) phonon has clearly decreased (softened). Fig. 2c shows the room temperature scattering at $\vec{Q}$ = (2, 5, 3), which corresponds to the zone boundary in the [ζ00] direction (X point). In this case the scattering centered at E = 0, whose width is instrumental in origin, is primarily due to the central component of the soft phonon spectrum, i.e., the central

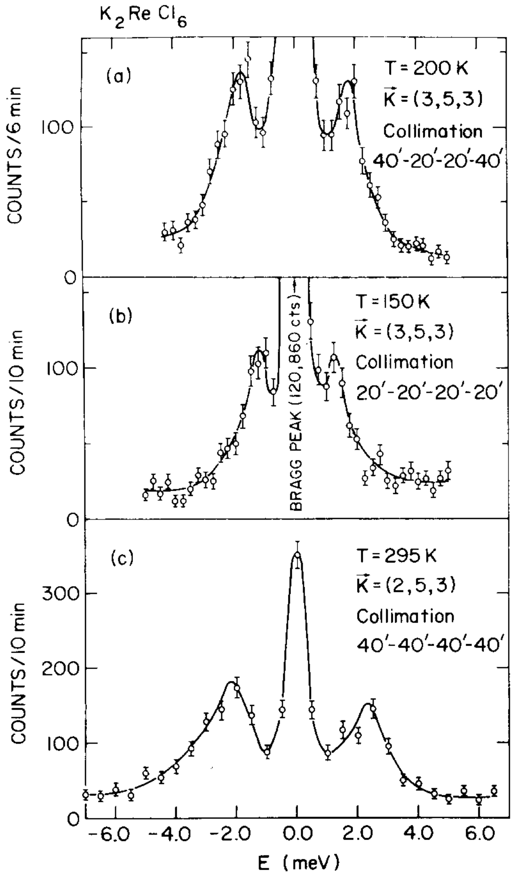

Fig. 2. Measurements of the soft rotary phonon at the zone center at a) 200 K; b) 150 K, showing that the phonon energy decreases as the transition temperature is approached; c) shows the observed scattering at the [100] zone boundary (X point) at 295 K.

peak. This central component is observed all along the [ζ00] direction with an intensity that increases upon approaching the transition. It is most intense, though, at the zone boundary point where the condensation at 103 K occurs. Similar diffuse scattering has also been observed in the related system K_2SnCl_6, but in that case the soft phonon was not observed.[8]

The energy of the soft phonon is shown in Fig. 3 as a function of wavevector along the [ζ00] direction. We see that there is very little dispersion in this direction, which signifies that the couplings within layers perpendicular to the rotation axis are strong compared to the interlayer couplings. The two-dimensional nature of these interactions is similar to that observed[9] for the F_6 octahedra in the perovskite $KMnF_3$.

As evidenced by the data in Fig. 2c, there is a considerable intrinsic linewidth to the phonons. As the transition is approached the entire [ζ00] transverse rotary branch softens, the phonons broaden in energy and the central component increases in intensity. The temperature dependence of the zone center and zone boundary phonon energies is given in Fig. 4. We see that the zone center phonon condenses first, driving the transition at 111 K, and then the zone boundary mode condenses at 103 K. This behavior is confirmed by measurements of the Bragg peak intensities. Below 111 K no new Bragg

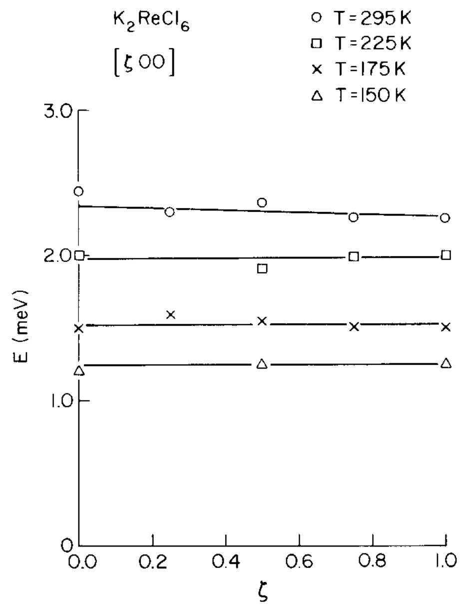

Fig. 3. The phonon dispersion relation for the transverse rotary mode along the [ζ00] direction at several temperatures. In the high temperature cubic phase there is very little dispersion, signifying that the interactions between Cl_6 octahedra are strongly anisotropic (two dimensional).

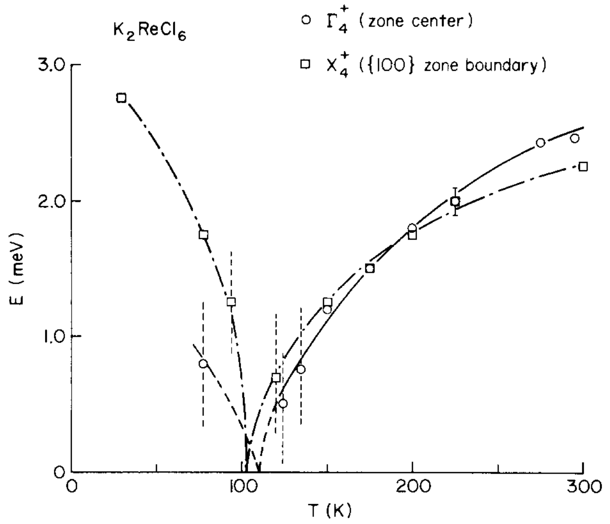

Fig. 4. The temperature dependence of the soft rotary mode at the zone center (solid circles) and the [100] zone boundary (open circles). The points with the dashed lines indicate that the phonon widths are comparable to their energies.

peaks are observed, but the intensities of the fundamental (cubic) peaks are strongly temperature dependent. Below 103 K new Bragg peaks develop at the {100} zone boundary positions in the high temperature phase. The qualitative features of these displacive transitions in K_2ReCl_6 are similar in some respects to the behavior observed[10] in $KMnF_3$, where successive condensations associated with rotations of the F_6 octahedra occur at the [110] and [111] zone boundary points.

The present data clearly demonstrate that the displacive transitions in K_2ReCl_6 are driven by the soft rotational mode of the $ReCl_6$ complex, confirming that this is the mechanism for these transitions in this class of antifluorite compounds. We note that the actual energy of the soft phonon (2.5 meV at room temperature) in the cubic phase is lower than that deduced by O'Leary and Wheeler (3.1 meV)[4] and van Driel, et al.[5] (5.7 meV) on the basis of NQR measurements. The analysis of the NQR data, however, depends on the accuracy of the lattice dynamical model, which is a complicated problem in the present case. The qualitative behavior of the soft mode is nevertheless given correctly. A more complete report of the lattice dynamics of these materials will be given elsewhere.

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