Soft rotary mode in the antifluorite crystal K_2OsCl_6

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Inelastic-neutron-scattering techniques have been used to study the structural phase transition in potassium hexachloro osmate (K_2OsCl_6). A low-frequency relatively flat phonon branch, identified to be the longitudinal-rotary mode, was observed in the [001] direction. This branch rises steeply in the perpendicular [350] direction indicating two-dimensional correlations in the motions of the $OsCl_6$ octahedra. Although the entire [001] branch softens as the phase transition is approached, it is the frequency of the zone-center phonon that exhibits the most rapid softening, consistent with its being the mode that triggers the structural transition. A simple damped-harmonic-oscillator analysis is presented.

I. INTRODUCTION

A neutron scattering study of the structural phase transition in the cubic-antifluorite crystal K_2OsCl_6 has been undertaken. Our earlier elastic-neutron-scattering results [1] indicated that the phase transition occurs at 44.5 ± 0.4 K and involves a ferro-rotation of the $OsCl_6$ octahedra. For the analogous transition in K_2ReCl_6 at 111 K, O'Leary and Wheeler [2] suggested that the zone-center rotary lattice mode should soften as T tends to T_c. In the present work we have searched for and found the particular rotary lattice mode which softens above T_c in K_2OsCl_6. The spectroscopy was carried out by means of inelastic-neutron scattering.

In what follows we describe the experiment, the temperature dependence of the dispersion curves obtained, and the damped-simple-harmonic-oscillator description of the rotary lattice mode observed above T_c.

II. EXPERIMENT

Two single crystals of K_2OsCl_6, with a total volume of $\sim 2\,cm^3$, were grown from aqueous solution [3] and aligned so that the scattering plane was $(\bar{5}30)$. Such a low-symmetry plane permits the simultaneous observation of the transverse and longitudinal-rotary modes; in high-symmetry planes such as (110) or (001), the structure factor for the longitudinal mode, whose eigenvectors are determined by symmetry, is everywhere zero. Note that our definitions of longitudinal- and transverse-rotary modes are the same as those of O'Leary and Wheeler[2], that is, in the longitudinal mode, the axis of molecular rotation is parallel to the wave vector.

Most of the experiments were carried out on the $L3$-triple-axis spectrometer at the NRU reactor, Chalk River. The monochromator and analyser were germanium (111) and pyrolytic graphite (002), respectively. For temperatures of 55, 65, and 70 K a higher resolution configuration was used to investigate the phonons. These experiments were done on the $N5$-triple-axis spectrometer at the NRU reactor. The (220) plane of silicon and the (111) plane of copper were used as the monochromator and analyser, respectively. For both sets of experiments the collimations were 0.6 ° and 0.7 ° before and after the specimen. Both spectrometers were operated in the constant-$\vec{Q}$ mode with fixed analyzer energies E_1 of 2.4, 2.6, or 3.0 THz.

III. DISPERSION CURVES

Measurements were made around (351) in the [001] and [350] directions. A typical set of scans for a wave vector (0,0,0.2) $2\pi/a$ is shown in Fig. 1. At high temperatures a well defined phonon peak is observed. As the phase transition is approached the phonon peak moves to lower frequencies and the quasielastic scattering grows in intensity.

The intensity in the phonon peak was found to be comparable everywhere between (351) and (353). At (351) no other phonon peaks are observed in the range $0 \leq \nu \leq 2$ THz. These observations lead to the identification of the mode as the longitudinal-rotary mode, for which the structure amplitude around (hk$l$),

$$h \sin(2\pi uk) - k \sin(2\pi uh)$$

is independent of l. This simple form of the structure factor exists because the eigenvectors of the

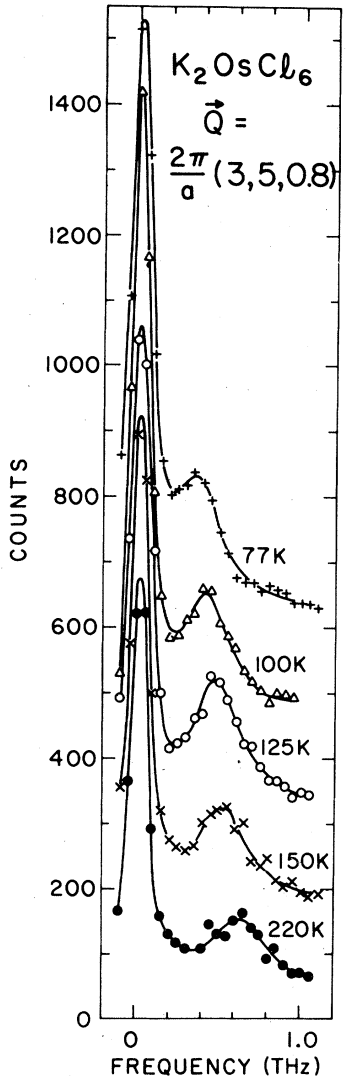

FIG. 1. Typical set of scans for a wave vector (3,5,0.8) $2\pi/a$. The temperature dependence of the longitudinal-rotary mode is evident.

[001] longitudinal rotary modes are uniquely determined by symmetry. [4] Confirmation of our assignment comes from results of a detailed lattice-dynamical calculation that we have performed, based on the O'Leary and Wheeler [2] model. We found that around (351) the structure factor for the transverse-rotary mode, which is the only other mode predicted to scatter appreciably, is relatively small.

A major feature of the longitudinal-rotary mode frequency (see Fig. 2) is that it exhibits little variation (less than 0.1 THz) along the [001] direction. The frequency $\nu(q_z)$ of the longitudinal-rotary mode for a wave vector $(0,0,q_z)$ is given by

$$4\pi^2\nu^2(q_z) = [2.42 + 2\cos(\tfrac{1}{2}q_z a)]\Phi_\perp/M_{\mathrm{Cl}} + \cdots ,$$

where the dots stand for terms independent of q_z plus the Coulomb term, M_{Cl} is the mass of a chlorine atom, and $\Phi_\perp$ is the perpendicular force constant between second-nearest-neighbor chlorine atoms on neighboring octahedra. A numerical calculation shows that the Coulomb term is essentially independent of q_z. The experimental result suggests that $\Phi_\perp$ is small, a reasonable result since the chlorine atoms involved are so far apart (4.9 Å).

A second interesting feature of the rotary branch is its strong anisotropy as a function of wave vector. Consider the rotary branch that corresponds to molecular rotations of the $OsCl_6$ octahedra about the [001] axis. For this atomic displacement pattern the frequency rises rapidly in the [350] direction as shown in Fig. 2. This result indicates that the coupling between [001] molecular rotations is strong within [001] layers but weak between layers. [5] Similar arguments may be applied to the modes corresponding to molecular rotations about [100] and [010]. This two-dimensional behavior of each of the [100], [010], and [001] rotary modes is not inconsistent with the measured three-dimensional character of the critical exponent β of the order parameter[1], because the simultaneous presence of the three orthogonal domains in this ferrosystem effectively re-

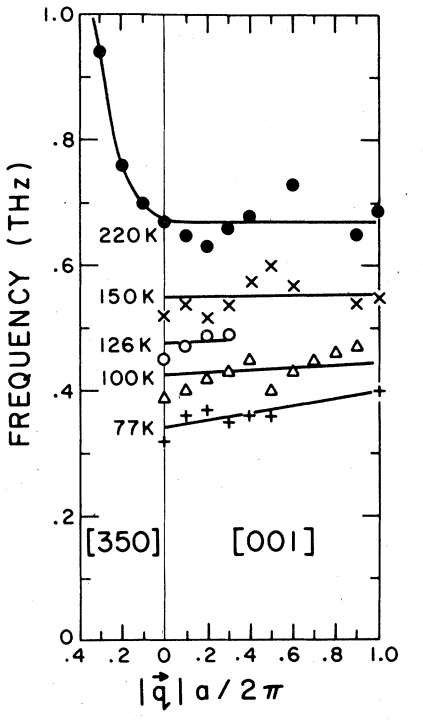

FIG. 2. Dispersion curves of the longitudinal-rotary mode at several temperatures. Note that there is very little frequency variation along the [001] direction and that the entire branch softens as the temperature decreases.

stores the cubic symmetry.

A third important characteristic of the rotary branch is that substantial softening occurs all along the [001] direction as the transition temperature is approached. The modes near the zone center exhibit the most rapid temperature dependence, however, and are the first to become overdamped. This suggests a ferrorotative symmetry change consistent with that observed previously in the structure work. [1]

IV. DAMPED-HARMONIC-OSCILLATOR ANALYSIS

Since the phonons were found to be broad compared to the experimental resolution and since the entire branch was temperature dependent, an analysis in terms of a classical-damped-harmonic oscillator[6] was undertaken. The scattering intensity at frequency ν for such a model is given by

$$I(\nu)=\frac{2C\Gamma\nu n(\nu)}{(\nu_O^2-\nu^2)^2+4\nu^2\Gamma^2}+B \ ,$$

where B is the background, C is the scale factor, Γ is the damping constant, $n(\nu)$ is the population factor $[1-\exp(h\nu/kT)]^{-1}$, and ν_O is the frequency of the undamped oscillator. A Landau-like dependence of ν_O on Γ was assumed

$$\nu_O^2=A(T-T_O) \ .$$

To compare with the experiment, the phonon line shape was folded with a gaussian whose width matched that of the measured vanadium width (0.08 THz at E_1 = 2.4 THz. The data above and below 77 K were fitted with independent scale factors and backgrounds since they were obtained under different experimental conditions. The agreement between the model and the data is shown in Fig. 3 for $q=0$; the parameters for each q are given in Table I. The

TABLE I. Parameters deduced from the damped-harmonic-oscillator analysis.

$aq/2\pi$	A ($\mathrm{THz^2\cdot K^{-1}}$)	T_0 (K)	Γ (THz)
0	0.019 ± 0.001	41 ± 2	0.16 ± 0.01
0.1	0.018 ± 0.001	29 ± 2	0.20 ± 0.01
0.2	0.017 ± 0.001	19 ± 4	0.20 ± 0.01
0.3	0.016 ± 0.001	13 ± 4	0.15 ± 0.01
0.4	0.017 ± 0.001	13 ± 5	0.14 ± 0.01
0.9	0.017 ± 0.001	7 ± 6	0.17 ± 0.01

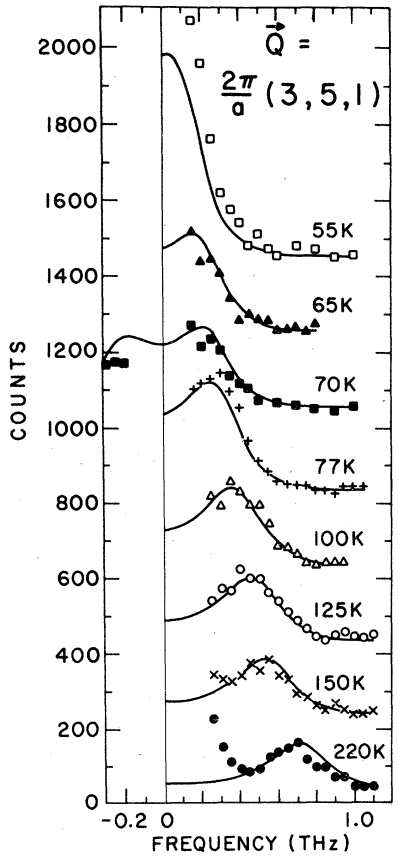

FIG. 3. Comparisons between the experimental data and the damped harmonic oscillator fits. A Landau-like dependence of ν_O on T was assumed.

results for T_O show that it is indeed the instability of the zone-center phonon that triggers the phase transition. The difference between the derived T_O associated with the zone-center phonon ($T_O=41\pm2$ K) and the value of T_c = 45.5 K obtained from our structural study, suggests that the Landau-like behavior breaks down close to the transition. Figure 4 shows the temperature dependence of the harmonic phonon frequency derived from the fitting.

In addition, temperature-dependent quasielastic scattering was observed for all wave vectors along [001]. Figure 1 shows a typical example at $(0,0,0.2)2\pi/a$. The number of counts at $\nu=0$ increases as the temperature decreases, whereas the intensity of the Bragg peak decreases. This scattering cannot be accounted for by the increase in intensity resulting from the softening of the longitudinal-rotary-lattice mode as given by the above damped-oscillator analysis. However, one should beware of interpreting this quasielastic scattering as a central peak. The scattering may well be elastic incoherrent scattering, which is large for Cl atoms and which also

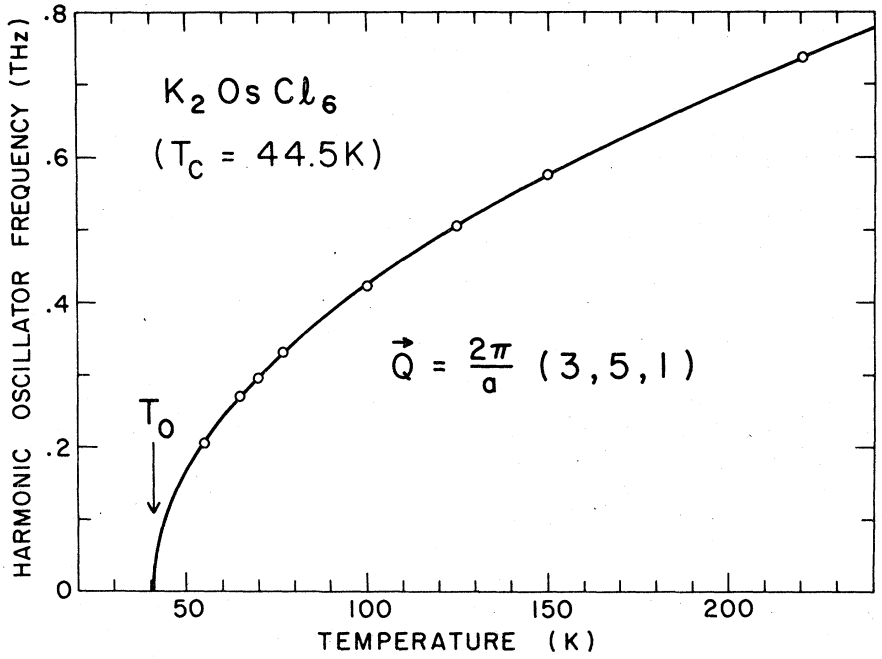

FIG. 4. Temperature dependence of the harmonic-phonon frequency derived from the damped-harmonic-oscillator analysis. The circles locate the temperatures at which measurements were made.

increases with decreasing temperature because of the Debye-Waller factor.

V. CONCLUSIONS

The entire longitudinal-rotary-lattice branch in the [001] direction has been found to soften in K_2OsCl_6 as the structural phase transition temperature is approached. The zone-center phonon exhibits the most rapid softening consistent with its being the mode that triggers the transition. The observed anisotropy of the dispersion of the longitudinal-rotary mode indicates two dimensional correlations in the motions of the $OsCl_6$ octahedra.

Simultaneously with this work, the analogous compound K_2ReCl_6 was studied.[7] The general behavior above the 111 K transition is remarkably similar to that reported here for K_2OsCl_6.

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