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Soft-mode behavior near the 111-K displacive phase transition in K_2ReCl_6 †

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It is shown that the geometrical model proposed to describe the high-temperature phase transition in K_2ReCl_6 is consistent with a rigid-ion-model calculation. In addition, the nuclear-quadrupole-resonance ^{35}Cl data taken in the cubic phase are analyzed to reveal a substantial softening of the zone-center rotary-lattice-mode frequency.

I. INTRODUCTION

O'Leary and Wheeler[1] (OLW) have presented the results of a comprehensive study of the compound K_2ReCl_6. At high temperatures the crystal structure is that of a cubic antifluorite compound; however, K_2ReCl_6 undergoes displacive phase transitions at 111, 103, and 76 K. Through a consideration of various kinds of experimental information OLW have shown that the most likely reduction in symmetry accompanying these transitions is

$$O_h^5 \xrightarrow{111\ \mathrm{K}} C_{4h}^5 \xrightarrow{103\ \mathrm{K}} C_{4h}^4 \xrightarrow{76\ \mathrm{K}} T_h^2 .$$

Further, they have deduced that the two highest temperature transitions result from the softening of the Γ^{15+} (referred to as Γ^{4+} in OLW) and X^{4+} rotary lattice modes, respectively. The two soft modes are optically inactive in the high-temperature phase; evidence of softening was deduced from the temperature variation of nuclear-quadrupole-resonance (NQR) frequency data. Neutron scattering experiments were not (and still are not) available to provide direct verification of these conclusions. Finally, OLW have constructed a rigid-ion model of K_2ReCl_6 which includes inter-octahedral ($ReCl_6$ -$ReCl_6$) interactions and have used the model to comment on the dynamics of the high-temperature phase transitions. In particular, they have shown that small changes in the inter-octahedral force constants could bring about a reduction in the rotary-mode frequency.

Brown[2] has introduced an empirical geometrical model for a number of compounds belonging to the R_2MX_6 family. From this model he has predicted which compounds undergo a tilting-type phase transition at room temperature, which distort at a lower temperature and which remain undistorted to 0 K. The lattice parameter in these compounds is primarily determined by the contact distance between the large MX_6 anions; this leaves cavities into which the R cations must fit. The important geometrical parameter is the ratio of the effective radius of the cation to that of the cavity. If this ratio decreases below a critical value as the temperature is lowered, the anions reorient to lock in the positions of the cations. This process may occur in several stages thereby giving rise to multiple-tilting-type phase transitions.

Lattice-dynamical theories of displacive phase transitions show that with each transition there is an associated soft librational mode. The librational-mode frequency for an R_2MX_6 compound depends to a large degree on the strength of the interaction between the X ions of the MX_6 anion and the R cations, and a reduction of the rotary-mode frequency might be expected to indicate a weakening and increasingly attractive interaction between the X and R ions. That this interpretation is consistent with the geometrical model has been verified quantitatively[3] in the case of K_2SnCl_6 by means of a molecular-orbital calculation.

The geometrical model suggests that the reduction of the rotary-mode frequency associated with the high-temperature phase transition in K_2ReCl_6

results from a weakening of the Cl-K interaction; the rigid-ion model calculation of OLW suggests that the reduction of the rotary-mode frequency results from a weakening of interoctahedral Cl-Cl interactions. The work reported in this note was undertaken in order to resolve this apparent discrepancy. In order to do this a computer program was written to calculate the dynamical matrix for K_2ReCl_6 for the rigid-ion model of OLW and to solve for the eigenfrequencies and eigenvectors of the normal modes. The dependence of the rotary-lattice-mode frequency at the zone center on the force constants of the model is discussed in Sec. II.

The analysis of the temperature variation of the NQR frequency data taken above 111 K in K_2ReCl_6 to yield evidence for the softening of the rotary mode as first suggested by O'Leary[4] later became the subject of some dispute.[5,6] In Sec. III of this note the NQR data are reanalyzed with the aid of the eigenvectors deduced from the computer program to provide convincing evidence for the softening of the rotary lattice mode.

II. DEPENDENCE OF ZONE-CENTER ROTARY-MODE FREQUENCY ON FORCE CONSTANTS IN RIGID-ION MODEL

In the OLW rigid-ion model of K_2ReCl_6 there are 14 independent parameters. Seven short-range interactions are considered; these are the Re-Cl, Cl-K, and K-K interactions, the nearest- and next-nearest-neighbor Cl-Cl interactions within a single octahedron and between different octahedra. Two parameters are required to specify each interaction; these are related to the first and second derivatives of the potential with respect to the atomic separation. Three effective charges for the Cl, K, and Re ions are used to describe the long-range Coulomb interactions. Charge neutrality eliminates one of the effective charges as an independent parameter. Two static equilibrium conditions further reduce the number of independent parameters, namely, that the crystal must be in a state of vanishing isotropic stress and that the force on a chlorine ion must be zero at equilibrium.

In order to deduce the force constants and effective charges for a cubic phase model of K_2ReCl_6 far from the phase transition, OLW determined 22 phonon energies at the center and edge of the Brillouin zone by making imaginative use of conventional spectroscopic techniques. Many of the phonon energies were measured in lower-temperature phases and it was necessary to assume that those energies were insensitive to temperature. No spectroscopic information concerning the rotary lattice mode was used in the fitting. The best set of parameters, in the least-squares sense, for this model (I) are presented in Table I. Using these parameters the rigid-ion model predicts a zone-center rotary-mode frequency of 46 cm^{-1}.

OLW considered another model (II) that could represent the K_2ReCl_6 structure near to a phase transition. In addition to the phonon energies used to obtain model-I parameters, this time they also fit to a zone-center rotary-mode frequency[7] of 26 cm^{-1}, much less than the value predicted by model I. Table I also lists the best set of model-II parameters. From a comparison of the two models, it can be seen that the force constants that change the most from model I to model II to permit the softening are interoctahedral ones (underlined in table). The small changes in the other force constants are required to satisfy the static equilibrium conditions in each case. A further consideration of the dispersion relations for the two models revealed that the X^{4+} mode is also sensitive to the changes related to going from model I to model II, thereby leading OWL to conclude that the phase transition at 103 K is driven by the softening of this mode.

The manner in which the rotary-mode frequency $\omega_{\Gamma 15^+}$ depends on the rigid-ion-model parameters is given by

$$\omega^2_{\Gamma 15^+} = (2/m_{Cl})(A_1 - B_1 + 2A_2) + \text{Coulomb terms},$$

where A_1 and B_1 are the parallel and perpendicular force constants associated with the potassium-chlorine interaction and A_2 is the parallel component of the interoctahedral chlorine-chlorine force constant identified by OLW as one of the force constants responsible for the 111-K phase transition in K_2ReCl_6. Since the Coulomb terms are not expected to be strongly temperature dependent, the softening of the rotary lattice mode must either re-

TABLE I. Lattice-dynamical model parameters for K_2ReCl_6.[a]

	Model I		Model II	
Charges (units of positive electronic charge)				
Re	0.40			
Cl	−0.32			
K	0.76			
Short-range force constants (10^3 dyn cm^{-1})				
Atom-pair	∥	⊥	∥	⊥
in same octahedron				
Cl-Re	131	14	130	14
Cl-Cl (nearest)	15	−2.7	16	−2.5
Cl-Cl (next-nearest)	31	−2.0	30	−2.6
Cl-K	6.7	−1.1	6.8	−1.2
K-K	0.66	•••	0.75	•••
in different octahedra				
Cl-Cl (nearest)	6.3	0.27	6.5	0.16
Cl-Cl (next-nearest)	0.67	−1.5	0.29	−1.5

[a]G. P. O'Leary and R. G. Wheeler, Phys. Rev. B 1, 4409 (1970).

flect a weakening of the particular Cl-Cl interaction or of the Cl-K interaction or the less likely simultaneous weakening of both. As can be seen from Table I, the Cl-Cl interaction is extremely weak even far from the phase transition because of the large separation between the two ions (~4.8 Å). This interaction, along with the K-K interaction, has the least sensitive parameters in the model.

To see if a softening of the rotary lattice mode could be achieved by a change in the Cl-K interaction, the effect of varying only A_1 and B_1 in the rigid-ion model I was considered. In order to do this, a computer program was constructed which permitted the calculation of the dynamical matrix for K_2ReCl_6 using the OLW rigid-ion model. From this result the eigenvalues and eigenvectors of the normal modes were determined and therefore the dispersion curves deduced. It is indeed possible to drive the zone-center rotary-lattice-mode frequency from 46 cm^{-1} to zero while not severely affecting the energies of the other modes. At the stability limit ($\omega_{\Gamma 15+} \sim 0$), the new values for the parallel and perpendicular Cl-K force constants are 2600 and 730 dyn cm^{-1}, respectively. The changes of these force constants from their high-temperature values (6700 and −1100 dyn cm^{-1}, respectively) are indicative of a weakening and increasingly attractive interaction.

Figure 1 indicates the dependence of the rotary-mode frequency and several other normal-mode frequencies on the two critical force constants. For other than the rotary-lattice mode, the variation of the mode frequencies is seen to be small. By making use of the many other degrees of freedom available within the model, one could maintain the other modes at relatively fixed values as the Cl-K interaction changes. In particular, the strict enforcement of the zero-stress lattice-equilibrium condition would hasten the softening of the rotary-lattice mode. That is, a smaller change in the Cl-K interaction would bring about the same softening with less change in the other normal-mode frequencies. However, this additional sophistication is unwarranted in the absence of detailed information concerning the temperature dependence of the normal modes and the lattice constant. In conclusion, the geometrical model of the high-temperature phase transition in K_2ReCl_6 is consistent with the OLW rigid-ion-model calculation.

III. ANALYSIS OF CHLORINE NQR FREQUENCY DATA ABOVE 111 K

Figure 2 shows the chlorine NQR data for K_2ReCl_6 taken for $T > 111$ K during the course of this work; they are consistent with the earlier data of O'Leary. These data are considered to be anomalous even apart from the fact that they may reflect some softening of the rotary-lattice-mode frequency. For most substances the increased averaging of the

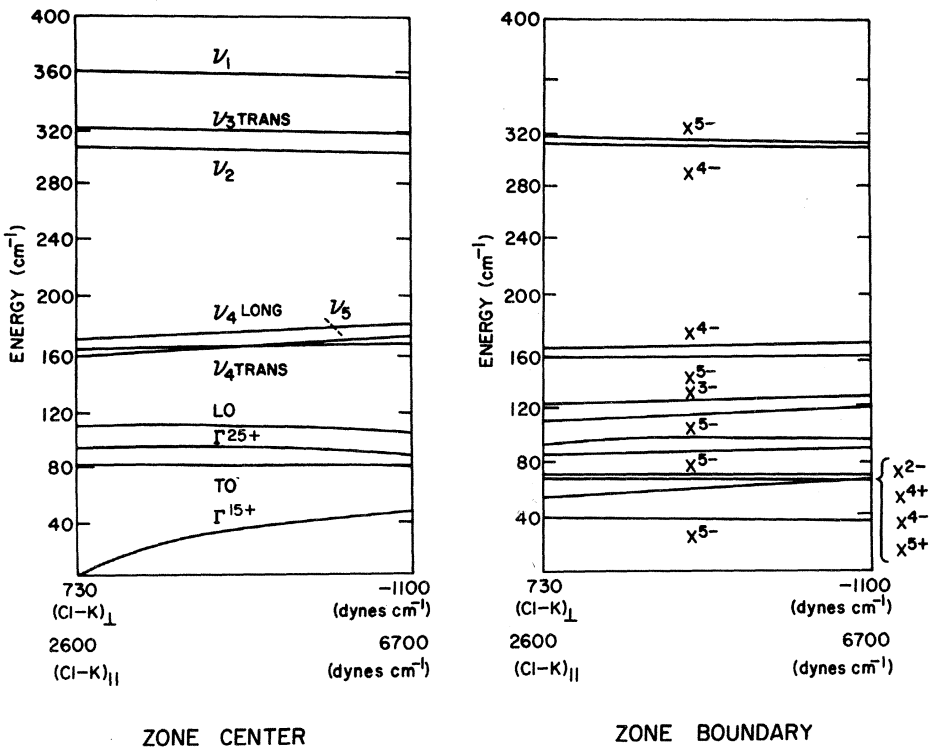

FIG. 1. Dependence of certain normal-mode frequencies of K_2ReCl_6 on the two critical force constants $(Cl\text{-}K)_\perp$ and $(Cl\text{-}K)_\parallel$. The horizontal scale is linear.

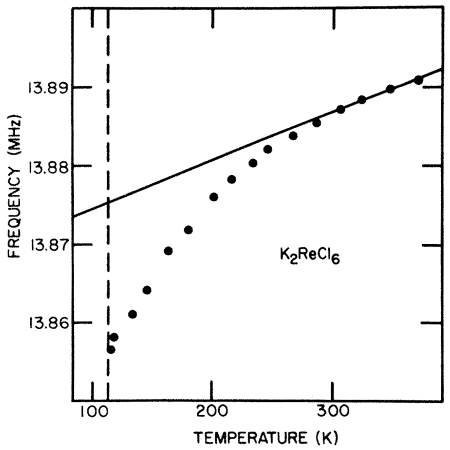

FIG. 2. Temperature dependence of the ^{35}Cl NQR frequency in K_2ReCl_6.

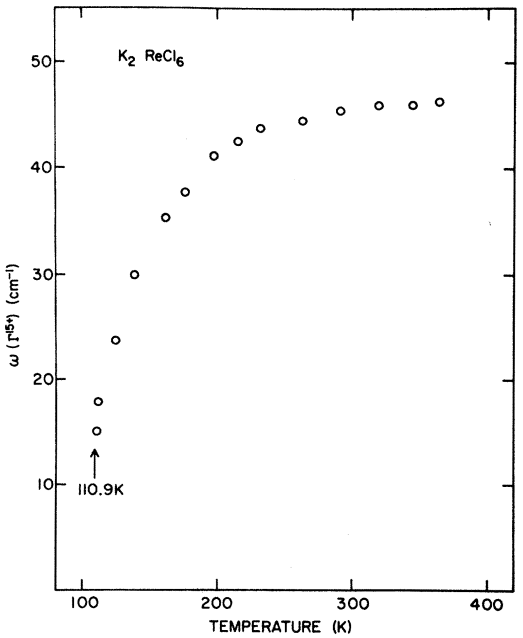

FIG. 3. Temperature dependence of the zone-center rotary-lattice-mode frequency as deduced from the ^{35}Cl NQR frequency data in the cubic phase of K_2ReCl_6.

electric field gradient with increasing temperature results in a decrease in NQR frequency; however, for K_2ReCl_6 the NQR frequency is seen to increase with increasing temperature. Haas and Marram[8] have attributed this sort of anomalous behavior to π-bonding effects. In K_2ReCl_6 there is a weak π bond, in addition to the strong σ bond, between the rhenium and chlorine ions. The increased thermal motions and the expansion of the Re-Cl bond length that are associated with an increased temperature cause a partial destruction of the π bond and an increase in the averaged electric field gradient experienced by a chlorine nucleus. In the presence of π bonding the temperature dependence of the NQR frequency is given by

$$\nu(T) = \nu_0(V, T)[1 - \tfrac{3}{2}\xi\langle\theta_x^2(T)\rangle - \tfrac{3}{2}\xi\langle\theta_y^2(T)\rangle] ,$$

where $\nu_0(V, T)$ is the static-lattice resonance frequency for volume V, temperature T, $\langle\theta_\alpha^2(T)\rangle$ is the αth component of the mean-squared angular displacement of the Re-Cl bond, which has its equilibrium orientation in the z direction, and the constant ξ provides a quantitative measure of the amount of π bonding. For the small changes in volume brought about by thermal expansion, $\nu_0(V,T)$ can be taken as a linear function of temperature so that

$$\nu(T) \simeq \nu_0'(1 + \chi T) - 3\xi\nu_0'\langle\theta_x^2(T)\rangle ,$$

with χ a constant. Assuming that

$$-3\xi\nu_0' \left.\frac{\partial\langle\theta_x^2(T)\rangle}{\partial V}\right|_T \ll \left.\frac{\partial\nu_0(V, T)}{\partial V}\right|_T ,$$

it follows that

$$-\frac{\alpha}{\beta}\left(\frac{\partial\nu}{\partial P}\right)_T = \chi\nu_0' ,$$

where α is the coefficient of thermal expansion and β is the isothermal compressibility. The assumption is reasonable since for the term on the left-hand side to be important the Grüneisen constants $\gamma(\vec{k}, j)$ would have to be unusually large, that is, $\gamma(\vec{k}, j) > 100$. Experiments[5,6] have provided the values $(\partial\nu/\partial P)_T = -0.0112$ kHz kg cm^{-2} and $\alpha/\beta = 39.0$ kg cm^{-2}K^{-1} near 300 K. A linear fit to the NQR data above 275 K (Fig. 2) provides the value ν_0' = 13.868 MHz. The value of χ is therefore determined to be 3.19×10^{-5} K^{-1}.

To determine ξ, the value $\langle\theta_x^2(T)\rangle$ must be known at some temperature. This quantity can be calculated at 300 K from the eigenvalues and eigenvectors of the rigid-ion model referred to in Sec. II using the expression[1]

$$\langle\theta_x^2(T)\rangle = \frac{\hbar}{2NR^2}\sum_{\vec{k}j}\left|\frac{e_x(\kappa_1|\vec{k}j)}{m_{\kappa_1}^{1/2}} - \frac{e_x(\kappa_2|\vec{k}j)}{m_{\kappa_2}^{1/2}}\right|^2 \coth\left(\frac{\hbar\omega_j(\vec{k})}{2k_BT}\right)\frac{1}{\omega_j(\vec{k})} = \sum_{\vec{k}j}\langle\theta_{x\vec{k}j}^2(T)\rangle ,$$

where $e_x(\kappa|\vec{k}j)/m_\kappa^{1/2}$ is proportional to the displacement of atom κ in normal-mode $(\vec{k}j)$ of frequency $\omega_j(\vec{k})$, κ_1 stands for Re, κ_2 stands for Cl, N is the number of molecules per unit volume, and R is the

Re-Cl bond length. Through the application of the special points method[9,10] to the K_2ReCl_6 lattice it follows that

$$\langle\theta_x^2(T)\rangle = \frac{1}{4}\sum_j [\langle\theta^2_{x\vec{k}_1 j}(T)\rangle + 3\langle\theta^2_{x\vec{k}_2 j}(T)\rangle] ,$$

where $\vec{k}_1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})2\pi/a$ and $\vec{k}_2 = (\frac{3}{4}, \frac{1}{4}, \frac{1}{4})2\pi/a$. From this expression a value of $\langle\theta_x^2(T)\rangle = 3.47\times10^{-3}$ rad^2 results and therefore $\xi = 0.772$.

Now that values of the parameters χ and ξ have been deduced the NQR data can be analyzed to yield values of $\langle\theta_x^2(T)\rangle$ at other temperatures. The lattice-dynamics computer program was then used to determine the temperature dependence of the zone-center rotary-mode frequency required to reproduce the $\langle\theta_x^2(T)\rangle$ values. The fitting, as achieved by allowing the Cl-K interaction to weaken, is shown in Fig. 3. It may be seen that the zone-center rotary-mode frequency softens from 46 cm^{-1} at 300 K to 15 cm^{-1} at 111 K. The actual amount of softening and the numerical values of $\omega_{\Gamma 15^+}$ depend upon the value of $\langle\theta_x^2(T)\rangle$ calculated at 300 K. This result in turn strongly depends on the ability of OLW model I to predict the rotary-lattice-mode dispersion curve at 300 K. However, even if the actual dispersion curve is significantly different from that predicted, the same qualitative behavior would result. In conclusion, the NQR ^{35}Cl frequency data have been analyzed to reveal a substantial softening of the zone-center rotary-lattice-mode frequency.

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[7]This is the observed low-temperature (1.6 K) value. Any value less than 46 cm^{-1} could have been used to investigate the effect on the force constants of a softening of the Γ^{15+} rotary mode.

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