SOFT LIBRATIONAL MODE DETECTION VIA NUCLEAR QUADRUPOLE RESONANCE*

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The temperature variation of pure nuclear quadrupole resonance frequencies provides a new tool for the detection of soft librational modes in spectrographically inaccessible regions. Data taken on K_2ReCl_6 above its 110.9°K phase transition are presented and are shown to imply a marked temperature dependence of the frequency of the $k=0$ rotary mode.

It has been suggested recently that nuclear quadrupole resonance (NQR) may be used to detect the presence of a low-lying librational mode. This possibility arises from the temperature variation of the mean-square nuclear displacement associated with such a mode. We will present experimental results which demonstrate the anamolous temperature dependence of the soft librational mode in K_2ReCl_6 and will comment on some aspects of the analysis presented in the paper by Jeffrey and Armstrong (JA).[1] Some of the unpublished results of the work of O'Leary and Wheeler (OW) will be presented as an aid to the present discussion.[2]

The NQR frequency for a nucleus of spin $I=\frac{3}{2}$ which is located at a crystallographic site possessing axial symmetry is given by $\nu=\frac{1}{2}eQq$, where Q is the nuclear quadrupole moment and q is the zz component of the electric-field gradient averaged over the thermal motion of the nucleus. This time averaging comes from the fact that the frequencies of the lattice vibrations are many orders of magnitude higher than the NQR frequency.[3] During one period of precession of the nuclear spin, the nucleus will oscillate many times about its equilibrium position. The gradient will respond essentially instantaneously to the nuclear displacements since it arises primarily from an orientation of the electronic orbitals of the atom in question. The lowest order nonzero time-averaged term of an expansion of the gradient in the nuclear motion will clearly be proportional to the mean-square displacement. The gradient, and thus the NQR frequency, will vary with temperature according to a weighted Debye-Waller factor involving the motions of the nucleus in question and the atoms which produce the gradient.

The relation between the nuclear motions and the gradient of the electric field is quite complicated in the general case. It is simplified considerably, however, if the following two approximations can be shown to be physically reasonable. The first requirement is that the major axis of the gradient point toward an origin, another atom, whose equilibrium position lies on the symmetry axis of the nucleus in question. The second is that the dominant thermal motion of the nucleus and the atom at the origin takes place in directions perpendicular to the symmetry axis. The lattice vibrational modes which involve motion along the symmetry axis must not be significantly populated at temperatures of interest. The assumption of axial symmetry forces the gradient to be at an extremum for motions perpendicular to the symmetry axis. Thus the lowest order effect of such motions will be to rotate the gradient without changing its magnitude.

In this approximation it is easily shown that the time-average gradient is given to lowest order by

$$q=q_0[1-\tfrac{3}{2}(\langle\theta_x^2\rangle+\langle\theta_y^2\rangle)], \tag{1}$$

where q_0 is the gradient in the absence of thermal motion and $\langle\theta_y^2\rangle, \langle\theta_x^2\rangle$ is the mean square angle of rotation of the bond axis about the y, x direction.[1,3] Therefore one would ordinarily expect that the gradient, and thus the NQR frequency, should decrease with increasing temperature due to the normal increase in population of the modes involving rotation of the bond axis. If, on the other hand, the vibration frequency of the dominant rotational mode should increase more rapidly than the temperature itself, the population of that mode would decrease with increasing temperature. This would result in an NQR frequency the temperature derivative of which is anomalously positive. Such a rapid temperature variation of the frequency of a rotational mode is just the behavior that is expected above the critical temperature of a soft librational-mode phase transition. Due to symmetry considerations, a librational mode in the high symmetry phase of such crystals is generally unobservable via infrared or Raman experiments. Thus nuclear quadrupole resonance provides a new and convenient tool for studying the temperature dependence of a soft mode in a previously inaccessible range of temperatures.

The nuclei of chlorine atoms in the fcc K_2MCl_6-type crystals provide an excellent example of nuclei for which the above conditions are satisfied. They form the corners of a regular octahedron surrounding the central metal ion with the M-Cl bonds pointing along the cubic crystal axes. The octahedra themselves form a fcc lattice and the potassium atoms occupy the tetrahedral interstices.[4] Thus the chlorine site symmetry is $C_{4v} = 4mm$. This symmetry is high enough to force the electric-field gradient to be symmetric about the unique axis.

Several pieces of evidence point to the fact that the chlorine is bound covalently to the metal atom and the other chlorines in the octahedron. The $MCl_6^{=}$ ion is stable in solution. It would certainly dissociate if the bonding were mainly ionic. Infrared-absorption[5] and Raman-scattering experiments done on the ions in solution[6] and in the solid[2] have verified that the frequencies of the molecular vibrations of the octahedron are insensitive to the crystalline environment. These frequencies change by less than 5% between the solution and the solid. Thus, the bonding of the chlorine which gives rise in the adiabatic approximation to the frequencies of the normal modes is determined primarily by the other atoms in the $MCl_6^{=}$ octahedron and only secondarily (on the order of 10%) by the surrounding atoms in the crystal. In addition, the magnitude of the NQR frequency, which is from 10 to 30 MHz in these crystals, can be explained only by assuming that the σ-bonding p_z orbital of the chlorine is partially empty.[7]

The final necessary assumption that the vibrational modes involving motion along the symmetry axis be insignificantly populated requires some comment. In JA it is argued that the Debye theta ($\theta_D > 200°K$) calculated from the specific heat[8] of these crystals is so high that the population of the acoustic mode will be much smaller than that of the low-lying librational mode. We wish to point out here, however, that while their conclusion as to the applicability of the technique is correct, their argument based on population alone is not. The results of a rigid-ion lattice-dynamics calculation for fcc K_2ReCl_6 done by OW indicate that the acoustic mode lies below the rotary Γ^{4+} mode nearly everywhere in the Brillouin zone. Thus the population of the acoustic mode will in fact be greater than the population of the librational mode. Note that a Debye theta represents contributions to the specific heat from all the degrees of freedom of the crystal and thus can be considerably higher in energy than the acoustic mode.

One must have some information about the eigenvectors of the normal modes before drawing conclusions about the effect of population. This information has been available in the literature for some time. The three internal modes which involve a change in the M-Cl bond length have energies lying between 275 and 360 cm^{-1}.[5,6] These energies are high enough to guarantee small populations of the stretching modes below room temperature. Alternatively one can say that the acoustic mode involves pure translation of the octahedron as a rigid body. It neither changes the M-Cl bond length, nor does it rotate the direction of the gradient. The acoustic mode has no effect on the NQR frequency.

Within these assumptions the mean square bending angle of the M-Cl bond, including the effects of the molecular bending vibrations as well as those of the rotary mode, is the dominant factor in the NQR frequency shift. This angle is given by

$$\langle \theta_x{}^2 \rangle = \frac{\hbar}{NR^2} \sum_{k,j} \left| \left[\frac{e_x(\mathrm{Cl}|{}^k_j)}{(M_{\mathrm{Cl}})^{1/2}} \right] - \left[\frac{e_x(M|{}^k_j)}{(M_M)^{1/2}} \right] \right|^2 \times \frac{\langle n({}^k_j) + \frac{1}{2} \rangle}{\omega({}^k_j)}, \tag{2}$$

where, for example, the eigenvector component $e_x(\mathrm{Cl}|{}^k_j)/(M_{\mathrm{Cl}})^{1/2}$, with eigenvalue $\omega({}^k_j)$, is the x displacement of the chlorine in the normal mode of wave vector k, and branch j; R is the M-Cl bond length; N is the number of molecules per unit volume; and $\langle n({}^k_j) + \frac{1}{2} \rangle$ is the Bose population factor. The eigenvectors of the internal modes can be estimated from the requirement that the center of mass of the octahedron remain stationary in the motion. For the rotary mode the coefficients, exclusive of the population factor and eigenvalue, reduce to $\hbar/I$, where I is the rotational inertia of the $MCl_6^{=}$ molecule. The population and eigenvalue involve a knowledge of the dispersion of the modes as a function of k. The dispersion of the three internal bending modes at 126, 166, and 172 cm^{-1} is small enough so that they can be treated adequately as triply degenerate Einstein modes.[9] The combined results of Eqs. (1) and (2) yield an NQR frequency shift of 0.4% at room temperature due to internal modes alone. This amounts to $\frac{1}{3}$ of the total frequency shift observed by JA in K_2PtCl_6 at room temperature. Therefore the contribution of these internal modes would seem to be important and should have been included in the analysis by JA.

The rotary mode presents a much more difficult problem of calculation than do the internal modes, due to its dispersion. The problem is especially acute at low temperatures where the Bose population factor in Eq. (2) must be treated exactly. At high enough temperatures or, equivalently, for low enough rotary mode energies, the population factor may be expanded as $\langle n(\begin{smallmatrix}k\\j\end{smallmatrix})+\frac{1}{2}\rangle \cong k_BT/\hbar\omega(\begin{smallmatrix}k\\j\end{smallmatrix})$. In this approximation the NQR frequency shift resulting from the rotary mode will reduce to $\Delta\nu_{\rm rot}/\nu_0 = 3k_BT/I\bar{\omega}^2$, where $1/\bar{\omega}^2$ is the average reciprocal square frequency of the transverse and longitudinal branches of this mode.

A very interesting example is provided by the soft-mode phase transition of K_2ReCl_6 at 110.9 °K.[10] At this transition, the crystal distorts slightly into a tetragonal structure ($c/a = 1.003$) having the same number of molecules per unit cell as the fcc phase. All of the spectrographic evidence collected thus far indicates that this transition occurs as a result of the softening of the $k=0$ rotary mode. The tetragonal phase then is characterized by a small ferrorotation of the $ReCl_6^{=}$ octahedra about the c axis. Our low-temperature Cl^{35} NQR data shown in Fig. 1 confirm the existence of this structure between 103.4 and 110.9°K. The Cl^{35} resonance splits into two lines which have an intensity ratio of 2:1. This corresponds to the fact that the chlorine nuclei lying along the z axis are no longer equivalent to those along the x and y axes. The continuous nature of the splitting of the resonance implies that the octahedral rotation angle (the order parameter of the distorted phase) is also continuous. Thus the transition is of second order, in the sense defined by Landau,[11] and one would expect to observe evidence of the presence of the soft mode responsible for the transition.

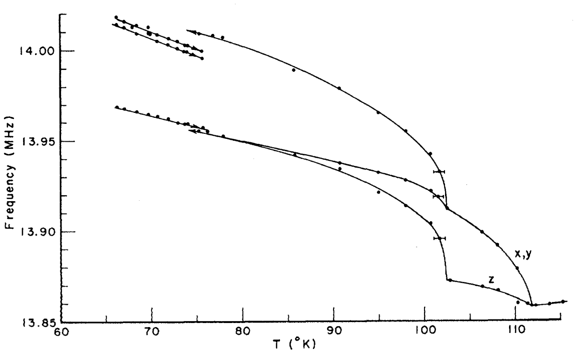

FIG. 1. Cl^{35} NQR frequency data taken on K_2ReCl_6 below the 110.9°K phase transition. Experimental error is ±1 KHz and ±0.25°K except as noted.

NQR frequency data taken on this salt above the transition are shown in Fig. 2(a). In light of the above discussion of the significant negative-temperature derivative produced by the internal modes, the direct observation of a positive derivative in the raw data indicates the dramatic nature of a temperature dependence of the soft rotary mode. Figure 2(b) shows a plot of $\bar{\omega}^2 = 3k_BT\nu_0/I\Delta\nu_{\rm rot}$, where $\Delta\nu_{\rm rot}$ was determined by first subtracting the calculated internal-mode frequency shift from the raw data. $\bar{\omega}^2$ is very nearly linear in T and thus in essential agreement with the classical predictions for such transitions due to Landau.[11,12] In the 110.9°K transition, the phonons at and near the zone center approach zero energy while those near the zone edges remain at finite energies. When account is taken of the small density of states available near $k=0$, we find that the average frequency $\bar{\omega}$ translates into a $k=0$ rotary mode frequency which softens from ~25 cm^{-1} at 300°K to ~1 cm^{-1} at 112°K.

The above interpretation of the high-temperature NQR results in terms of a soft mode can be made more convincing by further consideration of the low-temperature data. The observation of a negative $(d\nu/dT)_P$ everywhere below the 110.9°K

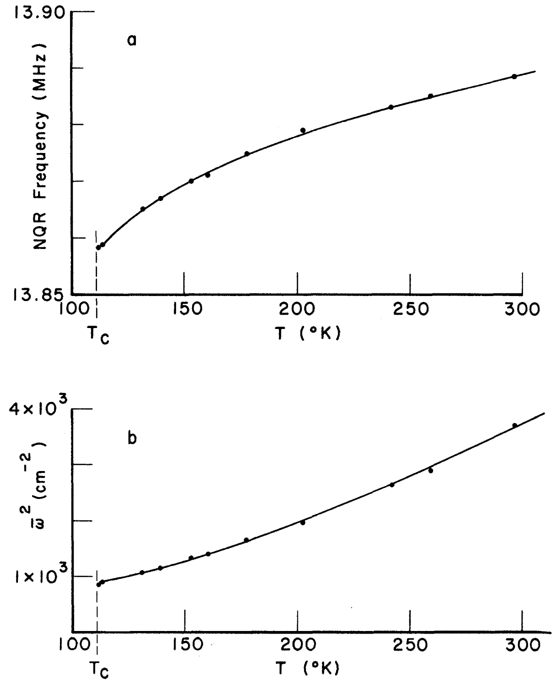

FIG. 2. (a) Raw Cl^{35} NQR frequency data taken on K_2ReCl_6 above the 110.9°K phase transition. Experimental error is ±1 KHz. (b) Plot of $\bar{\omega}^2$ (see text) with $\nu_0 = 14.050$ MHz determined by extrapolating data taken below transition to $T=0$.

transition can be used to argue against several alternative explanations for the high-temperature positive derivative. π bonding has been suggested as a possibility.[7] Optical studies, however, have established that the octahedron of chlorines is not distorted in the low temperature region.[9] Thus if π bonding were the cause of the anomalous behavior, one would expect to observe positive temperature derivatives at all temperatures. A second alternative is that the electric-field gradient itself might increase with increasing volume[13] so as to produce a positive temperature derivative of the NQR frequency. This description can be effectively answered by examination of the temperature region 103.4 to 110.9°K. Due to the tetragonal distortion of the axial lengths and the rigid-body nature of the ReCl_6 octahedron, the environment of the x and y chlorines moves toward them as one goes down in temperature while that of the z chlorine moves away. This motion corresponds to effective volume expansion for the x and y chlorines and a contraction for the z chlorine as one goes up in temperature. Note that the NQR temperature derivative for the x and y chlorines is in fact more negative than that for the z. Thus the volume dependence does have the normal sign to produce a negative temperature derivative of the NQR frequency. The volume dependence then is an additional factor to be overcome by the effects of the soft mode which results in the observed negative derivative.

In conclusion, we have clarified the necessary arguments for the applicability of NQR as a technique for measuring the Debye-Waller factor associated with a soft librational mode. These arguments apply to the $\mathrm{K}_2M\mathrm{Cl}_6$ system, thanks to the rigid-body nature of the $M\mathrm{Cl}_6^{=}$ octahedron. The data presented here result in the conclusion that the rotary mode in $\mathrm{K}_2\mathrm{ReCl}_6$ is strongly temperature dependent above its highest crystallographic phase transition. This is a result that could not have been obtained via spectrographic techniques because of the symmetry properties of the rotary mode.

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