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Softening of the Rotary Lattice Mode in K_2PtBr_6 as Detected by Nuclear Quadrupole Resonance*

Henry M. Van Driel,† Maria Wiszniewska,‡
B. Michael Moores, and Robin L. Armstrong
Department of Physics, University of Toronto, Toronto, Canada

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Measurements of the ^{79}Br nuclear-quadrupole-resonance frequency and spin-lattice relaxation time in a polycrystalline sample of K_2PtBr_6 from 4 to 450 K are reported. The frequency data indicate that structural phase transitions occur at 78, 105, 137, 143, and 169 K. The relaxation-time data are extremely sensitive to the phase transition at 169 K. At the high-temperature phase transition the structure of the substance changes from cubic to tetragonal. On the basis of previous comprehensive studies in K_2ReCl_6 it is likely that the phase transition is second order and is driven by the rotary lattice mode. As a model for this transition it is assumed that the $PtBr_6^{2-}$ octahedra remain undistorted but that they rotate within the cages defined by neighboring K^+ ions and that the cages elongate in the directions of the axes of rotation of the octahedra. The frequency data in the high-temperature phase are analyzed to yield the temperature dependence of a certain average $\bar{\omega}_\nu$ of the rotary-lattice-mode frequency over the Brillouin zone; a 12% softening is deduced. The relaxation data in the high-temperature phase are analyzed to yield the temperature dependence of a second average $\bar{\omega}_{T_1}$ of the rotary-mode frequency over the Brillouin zone; a 40% softening is deduced. It is shown that the difference between the temperature dependence of $\bar{\omega}_\nu$ and $\bar{\omega}_{T_1}$ is due to a difference in weighting of the rotary-mode frequency near the Brillouin-zone center. In particular, the dramatic temperature dependence of $\bar{\omega}_{T_1}$ can only be accounted for through the anharmonic Raman process and not the ordinary Raman process for quadrupolar-dominated spin-lattice relaxation. Below 169 K, two T_1 values, one approximately twice the other, are observed at each temperature. It is shown that this observation is consistent with the model postulated for the phase transition. The average rotary-mode frequency is found to harden as the temperature decreases below 169 K. That T_1 is insensitive to the phase transitions at lower temperatures is thought to imply that these transitions are not driven by the rotary-lattice mode.

I. INTRODUCTION

Nuclear-quadrupole-resonance (NQR) research carried out at the University of Toronto in recent years[1-5] to study the cubic R_2MX_6 compounds has shown that the temperature and pressure dependences of the resonance frequencies and spin-lattice relaxation rates of chlorine nuclei predominantly reflect the behavior of the low-lying rotary-lattice mode. Because of symmetry considerations this mode is neither infrared nor Raman active in the cubic phase, and therefore, NQR spectroscopy provides an especially attractive technique for the study of the rotary mode.

Many of the R_2MX_6 compounds exhibit multiple phase transitions from their high-temperature cubic phase to lower-symmetry phases as the temperature is decreased. It was suggested by O'Leary[6] that the temperature variation of pure-NQR-frequency data could be used to advantage for the observation of the softening of low-frequency librational modes in regions otherwise inaccessible to spectroscopic investigation. He presented data for the ^{35}Cl NQR in K_2ReCl_6 and analyzed the data in the region of the crystalographic phase transition at 110.9 K. The analysis of the experimental information for this paramagnetic compound is complicated by the possible contribution from π bonding and by large specific-volume effects.[3] To circumvent these difficulties we decided to study the ^{79}Br resonance in diamagnetic K_2PtBr_6 in which π bonding is not present and in which specific-volume effects are likely to be considerably less important.

Unfortunately, much less is known about the phase transitons in K_2PtBr_6 than in K_2ReCl_6. In our analysis we will rely on the results of the comprehensive analysis available for K_2ReCl_6.[7] In this salt the phase transition at 110.9 K is thought to be a displacive phase transition of the second kind in the Landau sense. According to the Landau theory the phase transition is brought about by the softening of an optical phonon at a particular point in the Brillouin zone. On the basis of a group-theoretical analysis all but three mode candidates can be eliminated. On the basis that the phase transition involves no change in the number of molecules per unit cell, two of the remaining three candidates can be rejected. The analysis predicts that the phase transition is driven by the softening of the rotary mode at the center of the Brillouin zone.

As well as measuring the ^{79}Br NQR frequency in K_2PtBr_6 it was also decided to measure the nuclear spin-lattice relaxation rate. The use of quadrupolar relaxation to study phase transitions, for example, ferroelectric ones,[8–10] is well known. We know of no previous experiment which has combined both NQR-frequency data and relaxation-rate data to study a single phase transition.

Previous NQR measurements in K_2PtBr_6 are limited to measurements of the ^{79}Br resonance frequency[11,12] at liquid-nitrogen, dry-ice, and room temperature and measurements of the ^{81}Br resonance frequency[13] at seven temperatures between 160 and 320 K.

II. 200-MHz SPECTROMETER

The measurements reported were obtained by means of a phase-coherent, pulsed, magnetic resonance spectrometer operating in the region of 200 MHz. A continuously operating signal generator centered at 200 MHz, stable to 1 part in 10^6, and having a bandwidth of 20 MHz provided the resonance frequencies. The rf pulses are produced using a gated MOSFET amplifier[14] which delivers 10 mW of peak power into a Hewlett Packard (HP) 230B power amplifier. The output from the HP 230B is further amplified in a power transmitter comprising a 6360 driver stage and a 3E29 output stage, both operating class C. The 1-kW rf pulses are coupled into the sample coil and the sample coil to the input of the receiver by means of a coaxial bridge circuit.[15] The receiver section consists of three dual-gate MOSFET preamplifiers. Phase-sensitive detection is achieved using a Hewlett Packard 1053A mixer detector. The coherent rf reference originates at the signal generator and is coupled to the HP 1053A via a General Radio trombone-line phase shifter. The detected output is further amplified in a video amplifier and then monitored on an oscilloscope or sampled by a boxcar integrator which drives a Moseley 7035B x-y recorder.

The sample coil forms part of a parallel L-C tuned circuit located within a Dewar. Impedance matching to the coaxial bridge is achieved by tapping at a suitable point on the coil. The $\frac{1}{2}\lambda$ coaxial line connecting the coil to the bridge consists of concentric, thin-walled, stainless-steel tubes chosen to make the characteristic impedance of the line 50 Ω. The variable capacitor (2–5 pF) consists of concentric conductors. The inner conductor which is movable, is grounded via a phosphor-bronze-wiper contact and is coupled to the outside of the cryostat through an O-ring seal.

III. EXPERIMENTAL PROCEDURE

The polycrystalline sample of K_2PtBr_6 was purchased from Atomergic Chemetals Co., Division of Gallard-Schlesinger Chemical Manufacturing Corp.

The auxiliary equipment for establishing and monitoring the temperature of the sample and the experimental techniques used to measure NQR frequencies and spin-lattice relaxation times have been described in an earlier publication.[16] The NQR frequency and spin-lattice relaxation time of the ^{79}Br nuclei in K_2PtBr_6 were measured at 5-K intervals from 4 to 450 K. Near the phase transitions, data points were taken at 1-K intervals. All temperature measurements are accurate to within 0.5 K, all NQR frequency determinations to within 10 kHz, and all spin-lattice relaxation time measurements to within 5%.

IV. TEMPERATURE DEPENDENCE OF THE NQR FREQUENCY

The $\nu(T)$ data for the ^{79}Br NQR of K_2PtBr_6 are shown in Fig. 1. From 450 to 169 K a single resonance line is observed; the frequency of the line increases by ~ 1.5 MHz as the temperature decreases over this range. Just below 169 K the line splits into two components with the intensity of the higher-frequency one (labeled $\nu_{x,y}$) being twice that of the lower-frequency one (labeled ν_z). The frequency of each line then increases as the temperature is further decreased. This behavior is compatible with the suggestion that the substance undergoes a displacive phase transition at 169 K from a high-temperature cubic structure to a structure possessing tetragonal symmetry. A second phase transition to a structure of still lower symmetry takes place at 143 K. Just below 143 K the high-frequency line splits into two components, and the three lines observed are of equal intensity. Below 143 K the frequency of the lower line increases uniformly as T decreases; the general trend of the upper line is similar; however, additional discontinuous changes are observed at 137, 105, and 78 K. Between 105 and 137 K the intensity of the single upper line is again twice that of the lower line. A recent x-ray determination[17] in this temperature range has confirmed that the structure is indeed tetragonal and that the number of formula units per unit cell is the same as in the high-temperature cubic phase. The observed splitting of the upper line between 78 and 105 K is ~ 50 kHz and

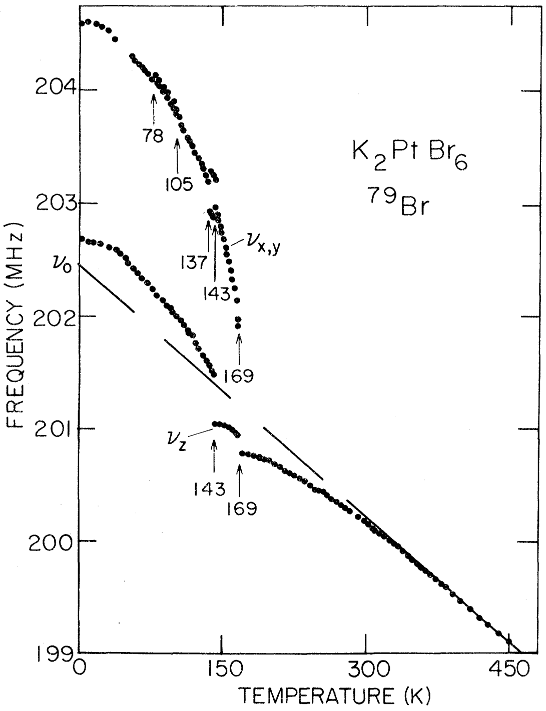

FIG. 1. Temperature dependence of the ^{79}Br NQR frequency in K_2PtBr_6. The data indicate that five phase transitions occur.

just within the resolution capability of the spectrometer.

The electric field gradient at a particular bromine nucleus in K_2PtBr_6 may be taken as the sum of two parts, a contribution q_{ci} from the complex ion to which the bromine nucleus belongs and a contribution q_{ni} from the neighboring ions, in particular, the K^+ ions, defining the cage in which the $PtBr_6^{2-}$ ion resides. The two contributions are of opposite sign, and the magnitude of q_{ni} is less than 10% that of q_{ci}.

One model for describing phase transitions in R_2MX_6 compounds[7] assumes that the MX_6^{2-} ions are rigid octahedral structures. In a phase transition the cage dimensions may change and the octahedra may reorient relative to the principal axes of the cage but the octahedra themselves remain unchanged.

The temperature dependence of $\nu(T)$ in the high-temperature phase reflects the increase with temperature of the efficiency of the lattice vibrations in averaging out the electric field gradient at the bromine nuclear sites. A detailed analysis of these data is presented below.

At 169 K a phase transition occurs. The angle of rotation of the equilibrium orientation of the $PtBr_6$ octahedra from that in the high-temperature cubic phase is taken as the order parameter for the phase transition. The observed splitting of the NQR line is associated with a change in the value of the order parameter. Theoretically, for a second-order phase transition, the order parameter changes continuously, from the value zero at the transition, as the temperature decreases from the transition temperature. In practice, however, the order parameter may experience a discontinuous change at the transition due to an increased interaction between those optical phonons which are driving the transition and the acoustic phonons. Therefore, the appearance of a discontinuous change in the NQR frequency at 169 K in the absence of hysteresis does not necessarily imply that the phase transition is of the first order. The temperature dependence of $\nu(T)$ below 169 K reflects both the temperature variation of the order parameter and the temperature variation of the efficiency of the lattice vibrations in averaging out the electric field gradient at the bromine nuclear sites. Similar qualitative remarks apply to each of the other phase transitions. No detailed analysis of the NQR-frequency data below 169 K is possible since we do not know how to separate the two contributions causing ν to vary with temperature.

If the model proposed to account for the phase transitions is a reasonable one then it must be able to account for frequency shifts of the order of 4 MHz due to changes in the magnitude of q_{ni} with the occurrence of the phase transitions. Since q_{ni} accounts for about 10% or 20 MHz of the observed frequency, changes in q_{ni} of the order of 25% are required. A simple calculation based on a point-charge model, and including only nearest neighbors, indicates that changes in the magnitude of q_{ni} of this amount are easily explained.

The analysis of $\nu(T)$ in the high-temperature phase was carried out using a procedure introduced by previous authors.[1,6] The electric field gradient at a bromine nuclear site possesses axial symmetry about the PtBr bond (z axis); the field gradient is assumed to arise entirely from the charge distribution within the complex ion. In this approximation the NQR frequency is given by

$$\nu(T) = eQq(T)/2h ,$$

where $eq(T)$ is the time-averaged value of the zz component of the electric-field-gradient tensor, and Q the quadrupole moment of the bromine nucleus. In lowest order

$$q(T) = q_0(1 - 3\langle \theta^2 \rangle) ,$$

where $\langle \theta^2 \rangle \equiv \langle \theta_x^2 \rangle = \langle \theta_y^2 \rangle$ is the mean-square angular displacement of the PtBr-bond axis in the x or y direction. From the theory of lattice dynamics in the harmonic approximation we find

$$\langle \theta_\alpha^2 \rangle = \frac{\hbar}{2NR^2} \sum_{\vec{k},j} \left| \frac{e_\alpha(\mathrm{Br} \mid \vec{k}j)}{m_{\mathrm{Br}}^{1/2}} - \frac{e_\alpha(\mathrm{Pt} \mid \vec{k}j)}{m_{\mathrm{Pt}}^{1/2}} \right|^2 \times \frac{\coth[\hbar\omega_j(\vec{k})/2k_B T]}{\omega_j(\vec{k})},$$

where $\alpha = x, y$; N is the total number of unit cells; $R = 2.63$ Å[18] is the PtBr-bond length; m_x is the mass of nucleus X; $e_\alpha(X \mid \vec{k}_j)$ is the αth component of the polarization vector associated with the displacement of nucleus X in the normal mode of branch j and frequency $\omega_j(\vec{k})$ at point $\vec{k}$ in the Brillouin zone. The summation is taken over the 15 internal modes of a $\mathrm{PtBr_6}^{2-}$ octahedron and the three rotary-lattice modes. Defining $\nu_0 = eQq_0/2h$ to be the static lattice resonance frequency, the frequency shift $\Delta\nu_{\mathrm{expt}}(T)$ from ν_0 at temperature T is

$$\Delta\nu_{\mathrm{expt}}(T) = \Delta\nu_{\mathrm{int}}(T) + \Delta\nu_{\mathrm{rot}}(T),$$

where

$$\Delta\nu_{\mathrm{int}}(T) = \frac{3\hbar\nu_0}{2NR^2} \sum_{j,\vec{k}}^{\mathrm{int\ modes}} \left| \frac{e_x(\mathrm{Br} \mid \vec{k}j)}{m_{\mathrm{Br}}^{1/2}} - \frac{e_x(\mathrm{Pt} \mid \vec{k}j)}{m_{\mathrm{Pt}}^{1/2}} \right|^2 \frac{\coth[\hbar\omega_j(\vec{k})/2k_B T]}{\omega_j(\vec{k})},$$

$$\Delta\nu_{\mathrm{rot}}(T) = \frac{2\hbar\nu_0}{2NR^2} \sum_{j,\vec{k}}^{\mathrm{rot\ modes}}{}' \left| \frac{e_x(\mathrm{Br} \mid \vec{k}j)}{m_{\mathrm{Br}}^{1/2}} \right|^2 \times \frac{\coth[\hbar\omega_j(\vec{k})/2k_B T]}{\omega_j(\vec{k})}.$$

A value for ν_0 was obtained from an extrapolation to $T = 0$ K of the straight-line fit to the data for $350 < T < 450$ K (see Fig. 1). The value $\nu_0 = 202.47 \pm 0.03$ MHz was deduced. The contribution $\Delta\nu_{\mathrm{int}}(T)$ is then evaluated assuming the normal modes of an isolated XY_6 molecule, neglecting dispersion, and substituting the vibrational frequencies found by Debeau and Poulet[19] for $(\mathrm{NH_4})_2\mathrm{PtBr_6}$. Although no infrared or Raman data are available for $\mathrm{K_2PtBr_6}$, the use of $(\mathrm{NH_4})_2\mathrm{PtBr_6}$ internal mode frequencies is justified since it is well established that these frequencies are quite insensitive to the crystalline environment. It is found that $\Delta\nu_{\mathrm{int}}(T)$ accounts for only about 10% of $\Delta\nu_{\mathrm{expt}}(T)$. The difference $\Delta\nu_{\mathrm{expt}}(T) - \Delta\nu_{\mathrm{int}}(T)$ is taken to be the contribution $\Delta\nu_{\mathrm{rot}}(T)$. From the above expression for $\Delta\nu_{\mathrm{rot}}(T)$ it follows that in the high-temperature approximation

$$\Delta\nu_{\mathrm{rot}}(T) = \frac{3\hbar\nu_0}{2NI} \sum_{\vec{k}} \frac{2k_B T}{\hbar\,\omega_{\mathrm{rot}}^2(\vec{k})} = \frac{3\nu_0 k_B T}{I} 4\pi V \int_k \frac{k^2 dk}{\omega_{\mathrm{rot}}^2(k)},$$

where I is the moment of inertia of the $\mathrm{PtBr_6}$ octahedron for oscillations about a principal axis, and V is the volume of the unit cell in the actual lattice. The integration is performed through one unit cell in the reciprocal lattice; the unit cell is approximated by a sphere. The neglect of the $\vec{k}$ dependence of the polarization vector is consistent with the model adopted for the field gradient. We define an average rotary-mode frequency

$$\overline{\omega}_\nu = \{4\pi V \textstyle\int_k [k^2 dk/\omega_{\mathrm{rot}}^2(k)]\}^{-1/2},$$

and write the expression for $\Delta\nu_{\mathrm{rot}}(T)$ in the form

$$\Delta\nu_{\mathrm{rot}}(T) = \frac{3\nu_0 k_B T}{I\overline{\omega}_\nu^2}.$$

Using this expression, the temperature dependence of $\overline{\omega}_\nu$ was deduced from the NQR-frequency data. Figure 2 shows the result obtained. As the temperature decreases towards the transition, $\overline{\omega}_\nu$ decreases. At 300 K, $\overline{\omega}_\nu(300) \simeq 32\ \mathrm{cm^{-1}}$, whereas at 169 K, $\overline{\omega}_\nu(169) \simeq 28\ \mathrm{cm^{-1}}$. That is, a 12% softening of the average frequency of the rotary-lattice mode is indicated.

V. TEMPERATURE DEPENDENCE OF THE NUCLEAR SPIN-LATTICE RELAXATION TIME

The $T_1(T)$ data for the ^{79}Br NQR of $\mathrm{K_2PtBr_6}$ are shown in Fig. 3. The most striking features of the data are the dramatic decrease in T_1 from ~40 msec at 30 K to 40 μsec at 169 K, a change of three orders of magnitude, and the pronounced T_1 minimum which coincides with the phase transition observed in the frequency data at 169 K. Above 169 K, the

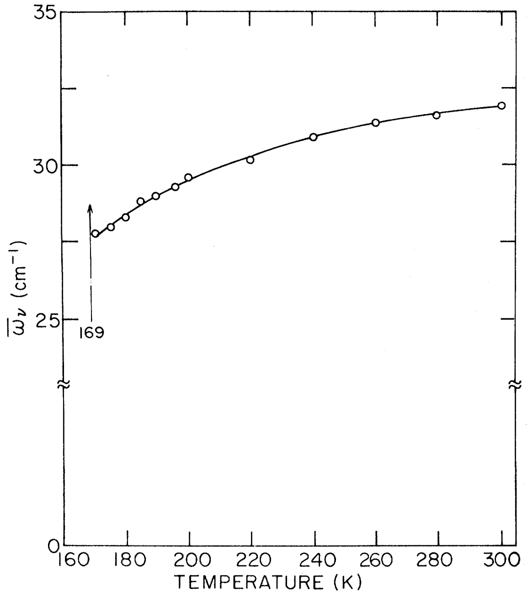

FIG. 2. Temperature dependence of the average rotary-mode frequency $\overline{\omega}_\nu$ as deduced from the NQR-frequency data in the high-temperature cubic phase. A 12% softening between 300 and 169 K is indicated.

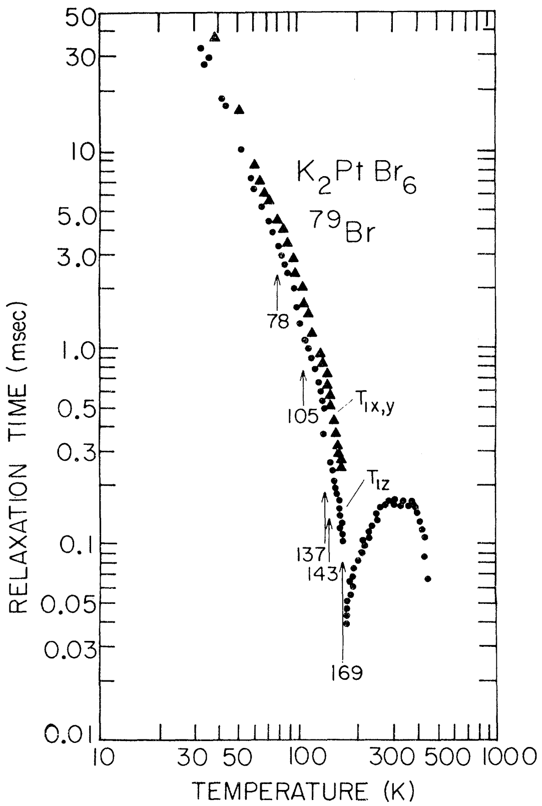

FIG. 3. Temperature dependence of the ^{79}Br spin-lattice relaxation time in K_2PtBr_6. Only the phase transition at 169 K is clearly apparent in the data.

single NQR line is characterized by a single relaxation time; below 169 K, the lines labeled ν_z and $\nu_{x,y}$ are characterized by spin-lattice relaxation times T_{1z} and $T_{1x,y}$, respectively, with $T_{1z} < T_{1x,y}$ at each temperature. The temperature at which the other phase transitions occur, as indicated by the frequency data, are marked on the diagram. There is little if any evidence for such phase transitions apparent in Fig. 3. In fact, the T_1's at any temperature as measured for the two upper lines in the temperature range $137 < T < 143$ K are somewhat different. For $78 < T < 105$ K, the T_1's for the two lines are indistinguishable to within experimental error.

Recent studies of chlorine nuclear spin-lattice relaxation in R_2PtCl_6 compounds[5,16,20] have shown that two relaxation mechanisms can be important—the resonant anharmonic-Raman process[21,22] and the nonresonant hindered-rotation process.[23] The latter process was identified in K_2PtCl_6 for $T > 320$ K by its characteristic isotope independence. We believe that it is this process which dominates the relaxation of the bromine nuclei in K_2PtBr_6 for $T > 400$ K and which is responsible for the rapid decrease of T_1 occurring at high temperatures. For the analysis presented below we assume that for $T < 300$ K the relaxation of the bromine nuclei is dominated by the resonant anharmonic-Raman process and consider that process only.

Initially, let us consider the relaxation-time data for $169 < T < 300$ K. In this range the crystal structure of K_2PtBr_6 is cubic, and the adaptation of the theory of Van Kranendonk and Walker[21,22] to R_2MX_6 substances are carried out by Armstrong and Jeffrey[20] should be applicable. Part of that presentation will be repeated here in order to clarify some of the steps taken. The relaxation rate of the bromine nuclei can be written as

$$T_1^{-1}(T) = \frac{29}{N^2} \sum_{\mu=1,2} \sum_{\vec{k}\vec{k}'jj'} \frac{4\pi Q^2}{3\hbar} \gamma_j(\vec{k})\gamma_{j'}(\vec{k}')$$

$$\times |f^{\mu}(\vec{k}\vec{k}'jj')|^2 n(\epsilon_j(\vec{k}))$$

$$\times [n(\epsilon_{j'}(\vec{k}')) + 1]\, \delta(\epsilon_{j'}(\vec{k}') - \epsilon_j(\vec{k}) - E_Q),$$

where $\gamma_j(\vec{k})$ is a microscopic Grüneisen parameter associated with mode j and wave vector $\vec{k}$, Q is the quadrupole moment of the ^{79}Br nucleus, $\epsilon_j(\vec{k}) = \hbar\omega_j(\vec{k})$ is the energy of a phonon labeled by $\vec{k}$ and j, n denotes a Bose-Einstein occupation number, E_Q is the energy difference between the NQR levels, and N is the total number of unit cells. The quantity $f^{\mu}(\vec{k}\vec{k}'jj')$ is defined by the relation

$$f^{\mu}(\vec{k}\vec{k}'jj') = \frac{\hbar}{2[\omega_j(\vec{k})\omega_{j'}(\vec{k}')]^{1/2}}$$

$$\times \sum_{\alpha,\beta} f^{\mu}_{\alpha\beta} \left(\frac{e_\alpha(\mathrm{Br}\,|\vec{k}j)}{m_{\mathrm{Br}}^{1/2}} - \frac{e_\alpha(\mathrm{Pt}\,|\vec{k}j)}{m_{\mathrm{Pt}}^{1/2}} \right)$$

$$\times \left(\frac{e_\beta(\mathrm{Br}\,|\vec{k}'j')}{m_{\mathrm{Br}}^{1/2}} - \frac{e_\beta(\mathrm{Pt}\,|\vec{k}'j')}{m_{\mathrm{Pt}}^{1/2}} \right),$$

where $f^{\mu}_{\alpha\beta}$ is the derivative with respect to x_α and x_β of the μth component of the electric-field-gradient tensor evaluated at the equilibrium position of the bromine nucleus. The summation is taken over the 15 internal modes of the $PtBr_6$ octahedron and the three-lattice modes. Introducing the high-temperature approximation and replacing $\sum_{\vec{k}\vec{k}'}$ by $(NV)^2 \int_{\vec{k}} \int_{\vec{k}} d\vec{k}\, d\vec{k}'$ gives

$$T_1^{-1} = 29 \sum_{\mu=1,2} \sum_{jj'} \frac{4\pi Q^2}{3\hbar} \frac{\hbar^2}{4}$$

$$\times \left| \sum_{\alpha,\beta} f^{\mu}_{\alpha\beta} \left(\frac{e_\alpha(\mathrm{Br}\,|\,j)}{m_{\mathrm{Br}}^{1/2}} - \frac{e_\alpha(\mathrm{Pt}\,|\,j)}{m_{\mathrm{Pt}}^{1/2}} \right) \right.$$

$$\left. \times \left(\frac{e_\beta(\mathrm{Br}\,|\,j')}{m_{\mathrm{Br}}^{1/2}} - \frac{e_\beta(\mathrm{Pt}\,|\,j')}{m_{\mathrm{Pt}}^{1/2}} \right) \right|^2 k_B^2\, T^2 V^2$$

$$\times \int_{\vec{k}} \int_{\vec{k}'} \gamma_j(\vec{k})\, \gamma_{j'}(\vec{k}')\, \frac{\delta(\epsilon_{j'}(\vec{k}') - \epsilon_j(\vec{k}) - E_Q)}{\omega_j^2(\vec{k})\, \omega_{j'}^2(\vec{k}')}\, d\vec{k}\, d\vec{k}'.$$

It should be noted that in accordance with the approximation of considering only nearest-neighbor coupling we have neglected the $\vec{k}$ dependence of the polarization-vector components.

Making the additional assumptions that $\omega(\vec{k})$ [and therefore $\gamma(\vec{k})$] is independent of the direction of $\vec{k}$ and that there is no significant overlap of the internal modes, the expression further reduces to

$$T_1^{-1}(T) = 29\left(\frac{4\pi Q^2}{3\hbar^2}\right) \sum_{\mu=1,2} \sum_{j,j'}{}' \frac{\hbar^2}{4}$$
$$\times \left| \sum_{\alpha,\beta} f^{\mu}_{\alpha\beta} \left(\frac{e_\alpha(\mathrm{Br}\,|\,j)}{m_{\mathrm{Br}}^{1/2}} - \frac{e_\alpha(\mathrm{Pt}\,|\,j)}{m_{\mathrm{Pt}}^{1/2}}\right)\right.$$
$$\times \left.\left(\frac{e_\beta(\mathrm{Br}\,|\,j')}{m_{\mathrm{Br}}^{1/2}} - \frac{e_\beta(\mathrm{Pt}\,|\,j')}{m_{\mathrm{Pt}}^{1/2}}\right)\right|^2 (4\pi)^2 k_B^2 T^2 V^2$$
$$\times \int_k \gamma_j(k)\gamma_{j'}(k') \frac{k^4\,dk}{\omega_j^2(k)\omega_{j'}^2(k)\,|\partial\omega_{j'}/\partial k|} .$$

The prime over $\sum_{jj'}$ denotes that the summation over j and j' contains nonzero contributions only for j and j' being degenerate branches of the same mode. Because of the relatively high frequencies of the internal modes their contribution to the relaxation rate is negligible[3] and $\sum_{jj'}$ need only include the rotary-lattice modes. Therefore, we find

$$T_1^{-1}(T) = 29\left(\frac{4\pi Q^2}{3\hbar^2}\right) \frac{\pi k_B^2 T^2}{m_{\mathrm{Br}}} \sum_{\mu=1,2} \sum_{jj'}^{\text{rot modes}} \frac{\hbar}{4}$$
$$\times \left| \sum_{\alpha,\beta} f^{\mu}_{\alpha\beta}\, e_\alpha(\mathrm{Br}\,|\,j)\, e_\beta(\mathrm{Br}\,|\,j') \right|^2$$
$$\times (4\pi)^2 V^2 \int_k \gamma_j(k)\gamma_{j'}(k') \frac{k^4\,dk}{\omega_j{}^2(k)\omega_{j'}{}^2(k)\,|\partial\omega_{j'}/\partial k|} .$$

The coefficients $f^{\mu}_{\alpha\beta}$ have been evaluated using a point-charge model. For the Pt nucleus located at (0, 0, 0) and the Br nucleus at $(0, 0, a)$ these coefficients are given by

$$f^1_{\alpha\beta} = \frac{3se}{R^5} \begin{vmatrix} 0 & 0 & -2 \\ 0 & 0 & -2i \\ -2 & -2i & 0 \end{vmatrix} ,$$

$$f^2_{\alpha\beta} = \frac{3se}{2R^5} \begin{vmatrix} 1 & 1 & 0 \\ i & -1 & 0 \\ 0 & 0 & 0 \end{vmatrix} ,$$

where e is the electronic charge, R is the PtBr-bond length, and s is a factor introduced to take account of covalency and antishielding effects. An estimate of s may be obtained from the NQR-frequency data through the expression

$$\nu(T) = (Q/2h)(2se/R^3) .$$

We then define an average rotary-mode frequency

$$\overline{\omega}_{T_1} = \left(\frac{(4\pi)^2 V^2}{\gamma^2} \int_k \frac{\gamma_{\mathrm{rot}}^2(k) k^4\, dk}{\omega_{\mathrm{rot}}^4(k)\,|\partial\omega_{\mathrm{rot}}(k)/\partial k|} \right)^{-1/5} ,$$

where γ is taken to be the average Grüneisen parameter for the rotary mode far from the phase transition. It is because the quantity on the right-hand side has the dimension of $(\text{time})^{-1}$ that we label the defined quantity an average frequency. The expression for the relaxation rate may then be written in the form

$$T_1^{-1}(T) = \tfrac{87}{4}(\pi\gamma Q s e k_B/\hbar m_{\mathrm{Br}} R^5)^2 (T^2/\overline{\omega}_{T_1}^5) .$$

Using this expression, the temperature dependence of $\overline{\omega}_{T_1}$ was deduced from the T_1 data. Figure 4 shows the result obtained for $\gamma \sim 2$. As the temperature decreases towards the transition, $\overline{\omega}_{T_1}$ decreases. At 300 K, $\overline{\omega}_{T_1}(300) \simeq 27$ cm^{-1}, whereas, at 169 K, $\overline{\omega}_{T_1}(169) \simeq 16$ cm^{-1}. That is, a 40% softening of the average rotary-mode frequency is indicated.

A comparison of $\overline{\omega}_\nu$ of Fig. 2 and $\overline{\omega}_{T_1}$ of Fig. 4 for $169 < T < 300$ K reveals that $\overline{\omega}_\nu$ exhibits substantially less softening than does $\overline{\omega}_{T_1}$. The sig-

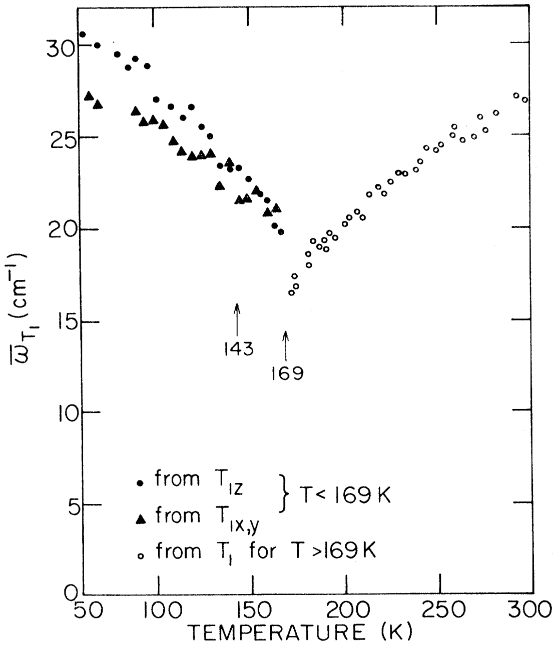

FIG. 4. Temperature dependence of the average rotary-mode frequency $\overline{\omega}_{T_1}$ as deduced from the spin-lattice relaxation-rate data. In the high-temperature cubic phase, a 40% softening between 300 and 169 K is indicated. The rotary mode hardens again as the temperature decreases below 169 K in the lower symmetry phase. For $143 < T < 169$ K, the $\overline{\omega}_{T_1}$ values deduced are, within experimental uncertainty, indistinguishable for z and for x, y nuclei.

nificance of this behavior will be discussed in Sec. VI.

Now we turn to a consideration of the relaxation-time data for $143 < T < 169$ K. Just below 169 K, the T_1 data change discontinuously and split into two components, labeled $T_{1x,y}$ and T_{1z} in Fig. 3 to identify them with the transition frequencies $\nu_{x,y}$ and ν_z, respectively, shown in Fig. 1. At each temperature in this range, $T_{1x,y} \simeq 2T_{1z}$. The explanation of this observation is as follows. As the temperature of the sample passes through 169 K from above, the crystal structure changes from cubic to tetragonal. In the tetragonal phase a unique z direction can be defined in the lattice with the result that nuclei on axes parallel to the z direction are not equivalent to nuclei in the xy plane. This inequivalence is reflected in both the frequency and spin-lattice relaxation-time data. As the lattice changes from symmetry class O_h to C_{4h} the rotary-lattice mode which was formerly triply degenerate at the Brillouin-zone center splits into components with frequencies $\omega_{x,y}(\vec{k})$ and $\omega_z(\vec{k})$, respectively. The theoretical expression developed above for the relaxation rate in the cubic phase can be easily adapted to describe the relaxation rates in the tetragonal phase. The reason for this is that according to the model proposed in Sec. IV to describe the phase transition, the $PtBr_6$ octahedra are not affected by the transition and the nearest-neighbor PtBr distance remains constant. That is, the observed change in T_1 with temperature is not influenced by the change in the order parameter. In the tetragonal phase, however, because of the splitting between the $\omega_{x,y}(\vec{k})$ branch and the $\omega_z(\vec{k})$ branch, scattering processes involving an incoming phonon corresponding to one of these branches and an outgoing phonon corresponding to the other give a substantially smaller contribution than do similar scattering processes in the cubic phase. Neglecting these processes, the relaxation rate for a z bromine nucleus can be written as

$$T_{1z}^{-1}(T) = \frac{87}{4}\left(\frac{\pi\gamma Qsek_B}{\hbar m_{\mathrm{Br}}R^5}\right)^2 \frac{T^2}{(\overline{\omega}_{x,y})_{T_1}{}^5}$$

and for an xy nucleus as

$$T_{1x,y}^{-1}(T) = \frac{87}{16}\left(\frac{\pi\gamma Qsek_B}{\hbar m_{\mathrm{Br}}R^5}\right)^2 T^2\left(\frac{1}{(\overline{\omega}_z)_{T_1}{}^5} + \frac{1}{(\overline{\omega}_{x,y})_{T_1}{}^5}\right)$$

in the tetragonal phase. Taking

$$(\overline{\omega}_z)_{T_1} = (1+\epsilon)(\overline{\omega}_{x,y})_{T_1}$$

it follows that

$$T_{1z}^{-1} = 2(1+\tfrac{5}{2}\epsilon)\, T_{1x,y}{}^{-1} .$$

Therefore, for $\epsilon \ll 1$ (as indicated in Fig. 4 for $143 < T < 169$ K) we find

$$T_{1z}^{-1} \sim 2\,T_{1x,y}^{-1}$$

in agreement with the experimental data.

Using the above expressions for $T_{1z}(T)$ and $T_{1x,y}(T)$, the temperature dependences of the respective average rotary-mode frequencies are as shown in Fig. 4. It is seen that the rotary mode again hardens as the temperature decreases from 169 K.

The insensitivity of T_1 to the presence of the other phase transitions is interpreted as evidence that they are not also driven by the softening of the rotary mode.

VI. INTERPRETATION OF THE DEDUCED $\overline{\omega}_\nu$ AND $\overline{\omega}_{T_1}$ VALUES

In Sec. IV we defined an average rotary-mode frequency

$$\overline{\omega}_\nu = \left\{4\pi V \int_k \left[k^2\, dk/\omega_{\mathrm{rot}}^2(k)\right]\right\}^{-1/2}$$

and deduced that this quantity decreased by ~12% as T decreased from 300 to 169 K. In Sec. V we defined a second average frequency

$$\overline{\omega}_{T_1} = \left(\frac{(4\pi)^2 V^2}{\gamma^2}\int_k \frac{\gamma_{\mathrm{rot}}^2(k)\, k^4\, dk}{\omega_{\mathrm{rot}}^4(k)\,|\partial\omega_{\mathrm{rot}}(k)/\partial k|}\right)^{-1/5}$$

and showed that this quantity decreased by ~40% as T decreased from 300 to 169 K. This difference may easily be understood in terms of the model proposed for the phase transition in which the frequency of the Γ-point rotary-mode phonons softens to zero at the transition. In order to calculate the two averages it is necessary to adopt a specific form for the dispersion curve. The dispersion curves shown in Fig. 5 and based on the earlier work in K_2ReCl_6 [7] are assumed. An approximate evaluation of $\overline{\omega}_\nu$ shows that a softening of ~12% over the temperature range considered is about what should be expected experimentally.

To calculate $\overline{\omega}_{T_1}$ we take

$$\gamma_{\mathrm{rot}} = \frac{V}{\omega_{\mathrm{rot}}}\,\frac{\partial\omega_{\mathrm{rot}}}{\partial V} \equiv \frac{V}{2\omega_{\mathrm{rot}}^2}\,\frac{\partial\omega_{\mathrm{rot}}^2}{\partial V} ,$$

where the variable V is a volume. The frequency

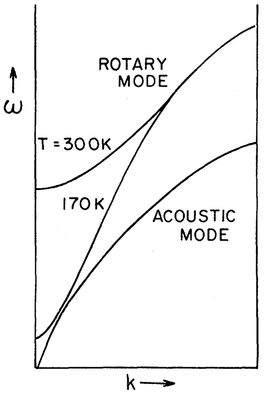

FIG. 5. Theoretical model for the dispersion curve of the rotary lattice mode at 300 and 170 K. The dispersion curve for the acoustic mode is also shown.

$\omega_{\rm rot}$ reflects the delicate balance between long-range and short-range forces experienced by the $PtBr_6$ octahedra. We may write

$$\omega^2_{\rm rot} = A/V^3 - B/V\,,$$

where each term on the right-hand side is much larger than their difference. At the transition temperature and at the Γ point the two terms exactly balance. By differentiation we find

$$-V\frac{\partial\omega^2_{\rm rot}}{\partial V} = \frac{2A}{V^3} + \omega^2_{\rm rot}\,,$$

which is a slowly varying function of T and k as compared to $\omega_{\rm rot}$. Therefore, we take

$$\gamma_{\rm rot} \propto 1/\omega^2_{\rm rot}$$

for the approximate evaluation of $\bar{\omega}_{T_1}$. A softening of ~40% is easily realized.

Finally, it is interesting to note that had we assumed that the ordinary Raman process, and not the anharmonic Raman process, provided the dominant relaxation mechanism, then the expression for the corresponding average rotary-mode frequency would have been

$$\bar{\omega}^0_{T_1} = \left((4\pi)^2 V^2 \int_k \frac{k^4\,dk}{\omega^4_{\rm rot}(k)\,|\,\partial\omega_{\rm rot}(k)/\partial k\,|}\right)^{-1/5}.$$

Using this expression and the dispersion curve shown in Fig. 5, the predicted softening of $\bar{\omega}^0_{T_1}$ is less than that of $\bar{\omega}_\nu$. Only by invoking a rather unlikely behavior of the dispersion curve near the Brillouin-zone boundary, can this expression account for the experimental observations. It is therefore felt that the present experiment offers substantial evidence in support of the generally accepted belief that it is the anharmonic Raman process and not the ordinary Raman process which dominates quadrupolar controlled spin-lattice relaxation.

VII. CONCLUSION

Data for the temperature variation of the ^{79}Br NQR frequency and spin-lattice relaxation time in K_2PtBr_6 in the vicinity of the structural phase transition occurring at 169 K have been analyzed in terms of a model introduced to describe the phase transition. The analysis shows that the model is self-consistent and adequate to account for the observations. We feel that the fact that both NQR-frequency data and relaxation-time measurements have had to be explained provides a significant test of the validity of the model. Many approximations have been introduced in order to carry out the analysis. Nonetheless, it is reasonable to expect that the treatment presented represents a satisfactory first-order approximation to a proper theoretical analysis.

Note added in proof. We have now carried out measurements of $\nu(T)$ and $T_1(T)$ for the ^{81}Br nucleus in K_2PtBr_6 for $143 < T < 300$ K. The results show that $\nu(^{79}\mathrm{Br})/\nu(^{81}\mathrm{Br}) = 1.1971 \pm 0.0001$ and that $T_1^{-1}(^{79}\mathrm{Br})/T_1^{-1}(^{81}\mathrm{Br}) = 1.4 \pm 0.1$ at all temperatures. The ratio of resonance frequencies provides an accurate measure of the ratio of nuclear quadrupole moments for the two isotopes. The ratio of relaxation rates (1.4) is equal to the square of the ratio of nuclear quadrupole moments $[(1.197)^2]$. This constitutes experimental proof that the observed relaxation is dominated by the resonant Raman process and not the nonresonant hindered rotation process in the region of the phase transition at 169 K.

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