

Cubic to tetragonal phase transitions in $(\text{NH}_4)_2\text{PtBr}_6$ and Rb_2PtI_6

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Nuclear-quadrupole-resonance data for the bromine and iodine nuclei in $(\text{NH}_4)_2\text{PtBr}_6$ and Rb_2PtI_6 have revealed a hitherto unreported type of cubic to tetragonal phase transition in R_2MX_6 compounds. These transitions are characterized by a tetragonal distortion of the lattice but no static rotation of the MX_6 octahedra. Several models for the specific physical nature of these transitions are discussed including both static and dynamic possibilities. The final identification must await another kind of experiment.

I. INTRODUCTION

The antiferroite (R_2MX_6) group of compounds is ideal for a systematic study of structural phase transitions. The large number of such compounds permits comparisons between family members varying in ionicity, lattice parameter, ion sizes, etc. However, the variety of phase transitions which occurs in these compounds is less than in the related perovskite (RMX_3) group, a simplification which is due to the much weaker interoctahedral interaction in the antiferroites.

For a typical compound of this family, the first phase transition to occur as the sample is cooled reduces the symmetry from cubic to tetragonal. Such a transition was first described in detail by O'Leary and Wheeler¹ who carried out a comprehensive study of K_2ReCl_6 . Their results may be summarized as follows: Upon cooling from room temperature, the rotary lattice mode softens and eventually freezes out at the transition temperature T_c ; that is, the lower-temperature phase is characterized by a static rotation of the ReCl_6 octahedra.² This rotation is accompanied by a small tetragonal distortion of the lattice. The rotation angle is the order parameter and the lattice distortion a necessary consequence. The phase transition is continuous.

This type-I model has subsequently been used to explain the cubic to tetragonal phase transitions in other R_2MX_6 compounds—notably^{3,4} K_2PtBr_6 and K_2OsCl_6 . It is the purpose of the present paper to show that the above behavior is not unique. Some R_2MX_6 compounds undergo another type of cubic to tetragonal transition. In the type-II case, the low-temperature phase is characterized by a tetragonal distortion of the lattice in the absence of a static rotation of the octahedra. The transition is of the first order. Such a transition occurs both in⁵ $(\text{NH}_4)_2\text{PtBr}_6$ and Rb_2PtI_6 .

II. THEORY

The identification of this second type of transition in the R_2MX_6 group follows from its distinctive nuclear-quadrupole-resonance (NQR) spectrum. The predicted features of this spectrum are apparent when the NQR frequency of the X nuclei is written in terms of the lattice distortion. This is most easily performed by expanding the frequency as a Taylor series about the cubic phase. Designating the frequency of X nuclei located on the α axis as ν_α , it follows that

$$\nu_\alpha = \nu_0(T) + \sum_{\beta} \delta_{\beta} \nu_{\beta}^{\alpha} + \dots,$$

where the dots indicate higher-order terms, δ_{α} is the change in the unit-cell dimension in the α direction

$$\nu_{\beta}^{\alpha} = \left. \frac{\partial \nu_{\alpha}}{\partial \delta_{\beta}} \right|_{\delta_x = \delta_y = \delta_z = 0},$$

and $\nu_0(T)$ is the NQR frequency that occurs if the cubic phase were stable at temperature T . The function $\nu_0(T)$ is a smooth continuous function of T .

By symmetry,

$$\nu_x^x = \nu_y^y = \nu_z^z = \nu_1$$

and

$$\nu_y^x = \nu_x^y = \nu_z^x = \nu_x^z = \nu_z^y = \nu_y^z = \nu_2.$$

If the z axis is the tetragonal axis and if volume changes are ignored, we may write

$$\delta_z = \delta, \quad \delta_x = -\frac{1}{2}\delta, \quad \delta_y = -\frac{1}{2}\delta,$$

and

$$\begin{aligned} \nu_z &= \nu_0(T) + \delta_x \nu_x^z + \delta_y \nu_y^z + \delta_z \nu_z^z + \dots \\ &= \nu_0(T) + \delta(\nu_1 - \nu_2) + \dots, \end{aligned} \quad (1)$$

$$\nu_x = \nu_0(T) - \frac{1}{2}\delta(\nu_1 - \nu_2) + \dots = \nu_y.$$

The result of physical interest is that the average frequency, defined as $\frac{1}{3}(\nu_x + \nu_y + \nu_z)$, is independent of the phase transition to first order in δ . That is, a tetragonal distortion of the lattice preserves the center of mass of the NQR spectrum of the X nuclei if the distortion is small and if volume changes are negligible. This prediction does not, however, preclude a large splitting of the individual resonance lines.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The experimental NQR frequencies of the bromine and iodine nuclei as a function of temperature for $(\text{NH}_4)_2\text{PtBr}_6$ and Rb_2PtI_6 are shown in Figs. 1 and 2, respectively. Both of these compounds are characterized by a single line at high temperatures. Upon cooling through the phase transition, this single line splits into two lines with an intensity ratio of 2:1. The more intense line is split upwards while the less intense line is split downwards by approximately twice as much. The centers of mass of these resonances are conserved within 6% of the total splitting. For comparison, the experimental plot for K_2PtBr_6 is shown in Fig. 3. Here, the center of mass is not even approximately conserved—both lines split upwards. In view of the qualitative difference between these spectra, it seems unlikely that the conservation of the center of mass of the NQR spectrum for $(\text{NH}_4)_2\text{PtBr}_6$ and Rb_2PtI_6 is accidental. It is more likely that it is indicative of the underlying symmetry of the tetragonal phase in these compounds. The deviation from exact conservation is probably due to volume effects and higher-order terms in the expansion.

Although the expression for the NQR frequencies was developed for the case of a static tetragonal dis-

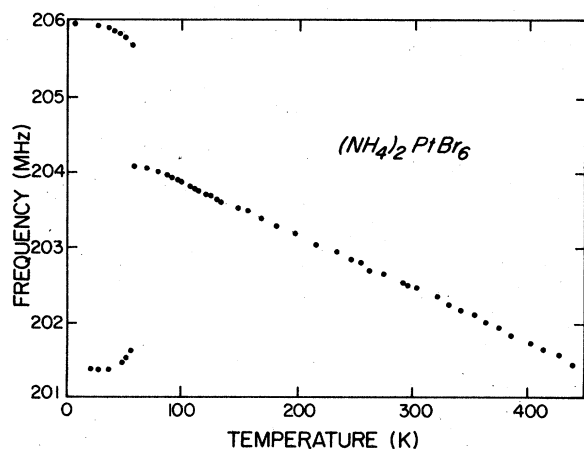


FIG. 1. Temperature dependence of the ^{79}Br NQR frequency in $(\text{NH}_4)_2\text{PtBr}_6$. Below the phase transition, the higher-frequency line is ν_x, ν_y , and the lower-frequency line is ν_z .

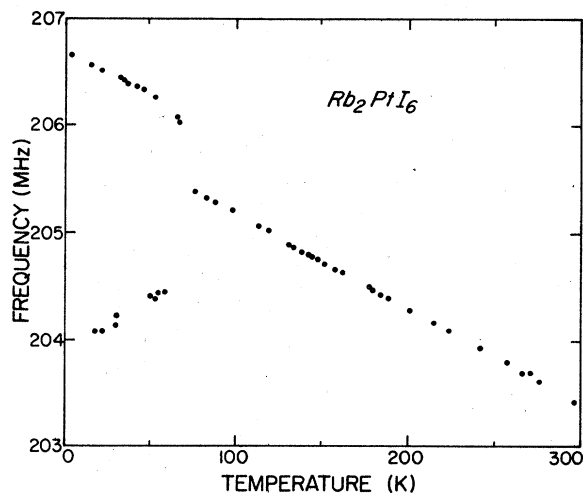


FIG. 2. Temperature dependence of the ^{127}I NQR frequency in Rb_2PtI_6 . Below the phase transition, the higher-frequency line is ν_x, ν_y , and the lower-frequency line is ν_z .

ortion of the lattice, the validity of Eq. (1) is dependent only upon the underlying symmetry of the low-temperature phase and not upon a specific model for the physical interpretation of the expansion parameter δ . For example, the assumption of a static tetragonal distortion of the MX_6 octahedra will lead to a similar expression. Alternately, a dynamic distortion associated with the removal of the threefold degeneracy of the rotary lattice mode at the zone center below the transition temperature will also give rise to an expression of the form of Eq. (1). Any one of these effects is capable in principle, of explaining the qualitative aspects

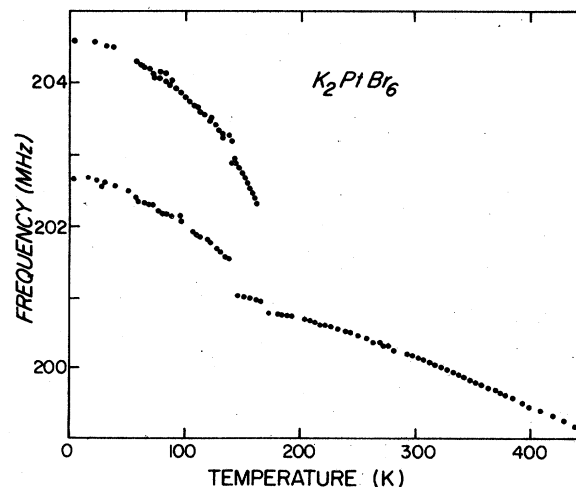


FIG. 3. Temperature dependence of the ^{79}Br NQR frequency in K_2PtBr_6 . Below the phase transition, the higher-frequency line is ν_x, ν_y , and the lower-frequency line is ν_z .

of the data. The dominant one will have to be selected by some other experiments. Either x-ray or neutron-scattering measurements would seem to offer the most promise.

IV. SOME GENERAL SPECULATIONS

The key to interpreting the magnetic resonance experiment is the size of the c/a distortion. That is, if $(c-a)/a$ is of the order of 0.02, the NQR splitting is consistent with the distortion of the lattice. However, in K_2ReCl_6 , $(c-a)/a$ has been measured to be 0.003. If this is indicative of the size of the distortion in $(NH_4)_2PtBr_6$ and Rb_2PtI_6 , it would appear to be much too small to be directly responsible for the observed splitting.

A second possibility is that the pure stretching mode corresponding to a tetragonal distortion of the MX_6 octahedra softens to precipitate the phase transition. But the spin-lattice relaxation data provide a strong argument against such an interpretation. Since this mode is a pure stretching mode, it should have no effect on the spin-lattice relaxation rate in first order. Experimentally, however, there is a significant relaxation anomaly at the phase transition. (Figs. 4 and 5) Furthermore, internal modes are usually insensitive to their environment—they are of high frequency and show little dispersion. It would be most surprising for such a mode to contribute to something as collective as a phase transition.

A third possibility is that there is a marked anisotropy in the motion of the MX_6 octahedra. This is possible even for small $(c-a)/a$ in the order-disorder limit. For example, assume that an octahedron must reside in one of six possible orientations—orientations

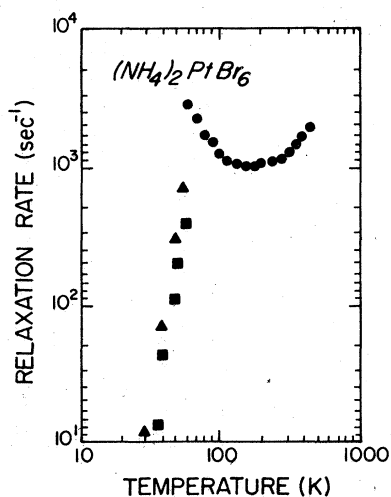


FIG. 4. Temperature dependence of the ^{79}Br NQR relaxation rate in $(\text{NH}_4)_2\text{PtBr}_6$. The two symbols used below the transition temperature refer to the two resonance lines.

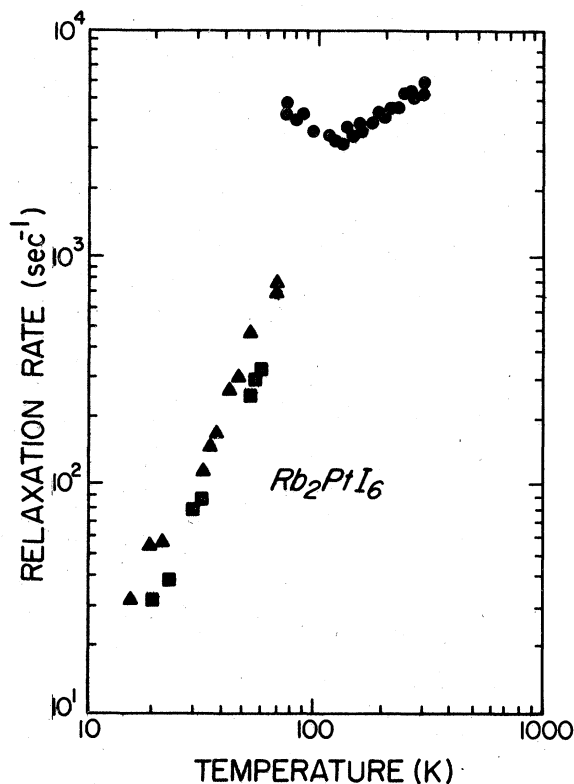


FIG. 5. Temperature dependence of the ^{127}I NQR effective relaxation rate in Rb_2PtI_6 . The two symbols used below the transition temperature refer to the two resonance lines.

corresponding to $\pm\theta$ rotations about the three crystal axes. The octahedral motion consists of hops from one orientation to another with the residence time per orientation being short on the NQR time scale. At a given instant, let the probability that the octahedron is rotated about the z axis be p . Then the probability that it is rotated about the x (or y) axis is $\frac{1}{2}(1-p)$. The symmetry of the cubic phase demands that $p = \frac{1}{3}$. No such restrictions apply to the tetragonal phase. If $\nu_0(0)$ and $\nu_0(\theta)$ are the NQR frequencies corresponding to nuclei in unrotated and rotated positions, respectively,

$$\nu_z = p\nu_0(0) + (1-p)\nu_0(\theta) = \frac{1}{3}[\nu_0(0) + 2\nu_0(\theta)] \\ + (p - \frac{1}{3})[\nu_0(0) - \nu_0(\theta)]$$

and

$$\nu_{x,y} = \frac{1}{3}[\nu_0(0) + 2\nu_0(\theta)] - \frac{1}{2}(p - \frac{1}{3})[\nu_0(0) - \nu_0(\theta)]$$

Note that in this case the quantity $p - \frac{1}{3}$ takes the place of the expansion parameter δ . If it is further assumed that the underlying potential is the same for

both type-I and type-II phase transitions, and taking $\theta \approx 5^\circ$ as deduced from the K_2PtBr_6 data, it follows that $\nu_0(\theta) - \nu_0(0) \approx 3$ MHz. These parameters are of the right order of magnitude to explain the results for $(NH_4)_2PtBr_6$ and Rb_2PtI_6 . The major difficulty with this order-disorder model is that the hopping about the z axis does not appear to freeze out at any temperature. This result would require that the zero-point energy be large with respect to the barrier to hopping which in turn would give a significant displacive character to the transition. That is, the transition would have to be intermediate between purely displacive and purely order-disorder.

The interpretation of spin-lattice relaxation data in the vicinity of a phase transition tends to be very model dependent. However, one important qualitative conclusion is possible in the present case. The general similarity of the relaxation data associated with type-I transitions (Fig. 6) and type-II transitions (Figs. 4 and 5) indicates that it is probably the same underlying mechanism responsible for both types of transitions. That is, both types of phase transitions appear to be precipitated by a softening of the rotary lattice mode. For type-I transitions the displacements are frozen in below T_c ; for type-II transitions they are not.

V. CONCLUSIONS

As a result of this work, a second type of cubic to tetragonal phase transition in R_2MX_6 compounds has been identified. In type-I transitions, the tetragonal

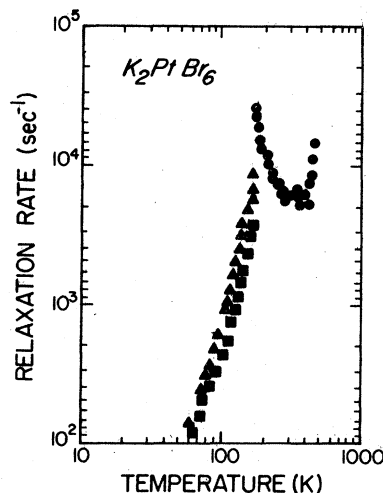


FIG. 6. Temperature dependence of the ^{79}Br NQR relaxation rate in K_2PtBr_6 . The two symbols used below the transition temperature refer to the two resonance lines.

phase is characterized by a static rotation of the MX_6 octahedra accompanied by a small distortion of the lattice; in type-II transitions the tetragonal phase is characterized by a tetragonal distortion of the lattice and no static rotation of the octahedra. The specific physical nature of the second type of transition has not as yet been elucidated. The dominant contribution to the distortion may be either static or dynamic. Other experiments are needed to resolve this question.

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