

Rb⁸⁷ Quadrupole Coupling and the Ferroelectric Transition in RbH₂AsO₄†

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The quadrupole-induced shifts of the Rb⁸⁷ $\frac{1}{2} \rightarrow -\frac{1}{2}$ NMR transition have been studied as a function of temperature and crystal orientation, and the electric-field-gradient (EFG) tensors at the Rb sites in RbH₂AsO₄ have been determined. In the ferroelectric phase there are two physically nonequivalent Rb⁸⁷ EFG tensors (*A* and *B*) which are related by the symmetry operations of the orthorhombic space group. In addition, each line is split into two components (*A*, *A'* and *B*, *B'*) because of domain effects. The Rb⁸⁷ quadrupole coupling constant equals 5.76 MHz at 108°K, and the asymmetry parameter is $\eta=0.85$. The paraelectric EFG tensor is nearly, though not exactly, equal to the average of the two ferroelectric ones (*A* and *B'*, or *A'* and *B*) from oppositely polarized domains. The anomalous decrease in the quadrupole coupling constant of Rb⁸⁷ with decreasing temperature in the paraelectric phase throws some light on the atomic motion as well as proton-lattice coupling and suggests that the Rb nuclei take part in collective atomic fluctuations which might represent an overdamped quasispin-wave ferroelectric mode.

INTRODUCTION

THE nature of the elementary excitations in KH₂PO₄-type hydrogen-bonded ferroelectrics is still not very well understood.¹⁻³ Whereas it is now generally accepted that the ferroelectric behavior and the dielectric,⁴ Raman scattering,⁵ thermal conductivity,⁶ NMR relaxation,^{7,8} and ultrasonic data^{9,10} can be described nearly as well either in terms of a very-low-frequency, strongly overdamped collective "ferroelectric" mode or in terms of order-disorder polarization fluctuations, interacting with an acoustic mode, conflicting evidence exists as to the nature of the elementary dipoles taking part in this motion. According to one point of view, the frequency of the protonic "quasispin-wave" mode¹—corresponding to collective proton motion between the two equilibrium sites in the *H* bonds—decreases with decreasing temperature in the paraelectric phase to such an extent that a "crossover" exists with a temperature-independent low-frequency

polar-lattice mode Ω of the same symmetry.¹¹ The frequency ω of the resulting coupled quasispin-wave-phonon mode—which is responsible for the ferroelectric behavior—is always smaller than Ω and goes to zero as one approaches the Curie point (T_c). The decrease in the frequency of the coupled ω_- mode in which the proton system and the lattice oscillate in phase (two protons move towards and two move away from a given PO₄ group, whereas the K and P atoms move in opposite directions along the *Z* axis) should thus result in an anomalous behavior in the mean-square vibration amplitude of the K and P atoms in the *Z* direction with decreasing temperature as one approaches the Curie point from above. The crystal structure of the ferroelectric state would then correspond to the "frozen-in" ω_- mode.

According to the second point of view, the proton motion in the paraelectric phase is so fast that no cross-overs between the proton and the low-frequency phonon branches exist, and the lattice cannot respond to the instantaneous proton arrangement. The proton system and the "lattice" are effectively decoupled¹² in the paraelectric state. The displacements of the K and P atoms relative to the oxygen network in the $+Z$ and $-Z$ directions, respectively—which account for the major part of the spontaneous polarization—occur only after the spontaneous ordering has taken place at T_c . Except for the immediate neighborhood of the Curie point, the motion of the lattice ions should not show any unusual temperature behavior or anisotropy.

Recently, still another model has been suggested¹³ according to which the potassium ions in KH₂PO₄ move along the *c* axis between two equivalent positions,

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¹ P.-G. de Gennes, *Solid State Commun.* **1**, 132 (1963).

² W. Cochran, *Advan. Phys.* **10**, 401 (1961).

³ For a review see A. S. Barker, Jr., in *Ferroelectricity*, edited by E. F. Weller (American Elsevier Publishing Co., Inc., New York, 1967), or R. Blinc, in *Proceedings of the International Course on The Theory of Condensed Matter, 1967* (to be published).

⁴ R. M. Hill and S. K. Ichiki, *Phys. Rev.* **130**, 150 (1961); I. P. Kaminow, *ibid.* **138**, A1539 (1965); see also F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

⁵ I. P. Kaminow and T. C. Damen, *Phys. Rev. Letters* **20**, 1105 (1968).

⁶ Y. Suemune, *J. Phys. Soc. Japan* **22**, 735 (1967).

⁷ H. B. Silsbee, E. A. Uehling, and V. H. Schmidt, *Phys. Rev.* **133** A165, (1964); V. H. Schmidt, *ibid.* **164**, 749 (1967).

⁸ R. Blinc and S. Zumer, *Phys. Rev. Letters* **21**, 1004 (1968).

⁹ E. Litov and E. A. Uehling, *Phys. Rev. Letters* **21**, 809 (1968).

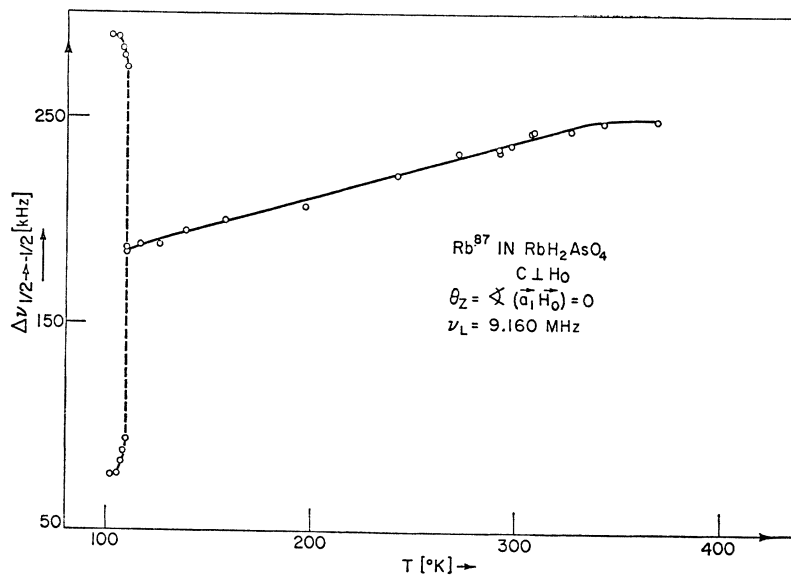
¹⁰ H. Z. Cummins and E. M. Brody (to be published).

¹¹ K. Kobayashi, *J. Phys. Soc. Japan* **24**, 497 (1968).

¹² H. Megaw, *Ferroelectricity in Crystals* (Methuen Ltd., London, 1957).

¹³ J. A. Krumhansl (private communication); S. Svetina (unpublished work from this laboratory).

FIG. 1. Quadrupole-induced shift of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ Rb^{87} NMR transition in an unpoled RbH_2AsO_4 crystal as a function of temperature.



and the proton-mediated potassium-potassium interactions trigger the phase transition.

No really convincing experimental test of the above models, with respect to the cation motion, has been made so far. Contrary to earlier suggestions of strong anisotropy based on x-ray data,¹⁴ neutron diffraction measurements of Bacon and Pease¹⁵ did not reveal any preferred direction of the thermal motion of the K and P atoms. In addition to this, the vibrational amplitudes as deduced from the intensities of the Bragg peaks show no unusual behavior and decrease when approaching the Curie point from above without exhibiting any critical effects. This evidence was considered to demonstrate the existence of a decoupled "stable" lattice and to support the second above-mentioned point of view. Recently, however, some doubts have been raised as to the correctness of this conclusion, since the purely elastic and the quasi-elastic scattering contributions have not been separated. Another objection is that temperature factors deduced from neutron diffractions represent an average over all normal modes of the lattice and are thus hardly suitable to yield information on the behavior of a single collective mode. The recent observation of strong critical quasi-elastic neutron scattering¹⁶ in KH_2PO_4 similarly does not favor the second above-mentioned point of view. Because of these discrepancies it seemed worthwhile to investigate the lattice dynamics of KH_2PO_4 -type crystals with an independent method which should be a more sensitive indicator of the cation motion and the possible existence of a coupled "proton-lattice" ω_- mode.¹⁷ We decided to use the quadrupole

moment of the Rb^{87} ($I = \frac{3}{2}$, natural abundance 27%) nucleus in RbH_2AsO_4 as a microscopic probe for the investigation of the temperature dependence of the electric-field-gradient (EFG) tensor at the Rb sites. The time average of the Rb quadrupole coupling constant is, namely, very sensitive to the charge rearrangements in the lattice and the relative motion of the Rb nucleus with respect to the surrounding oxygen network, so that a discrimination between the above-mentioned models should be possible. The As^{75} resonance has been measured as well, but these data will be referred to only in the discussion, since other groups have published or are in the process of publishing similar data.¹⁸

RESULTS

The quadrupole-induced shifts of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ magnetic-resonance transition of Rb^{87} have been measured as a function of temperature (Fig. 1) and crystal orientation at a frequency of 9.160 MHz.

In the paraelectric phase, the shift was found to be independent of the angle of rotation around the Z axis. The field-gradient tensor is thus axially symmetric ($V_{xx} = V_{yy} = -\frac{1}{2}V_{zz}$) for $T > T_c$ and the Z axis is a principal axis of the field gradient.

These results agree with the structural data.^{14,15} RbH_2AsO_4 is isomorphous with KH_2PO_4 , which crystallizes at high temperatures in the tetragonal space group $I4\bar{2}d$ with four "molecules" per unit cell. In the

(Ref. 10) have demonstrated that the ferroelectric mode is strongly coupled to an acoustic mode which becomes unstable at T_c as a result of the decrease in the frequency of the ferroelectric mode, but could not give any firm clues on the nature of the ferroelectric mode itself.

¹⁸ G. Cinader, D. Zamir, and I. Pelah, *Solid State Commun.* **6**, 435 (1968); W. Beezhold and E. A. Uehling, *Phys. Rev.* **175**, 624 (1968). J. L. Bjorkstam (private communication); A. P. Zhukov, I. S. Rez, V. I. Pakhomov, and G. K. Semin, *Phys. Status Solidi* **27**, K129 (1968).

¹⁴ B. C. Frazer and R. Pepinsky, *Acta Cryst.* **6**, 273 (1953).

¹⁵ G. E. Bacon and R. S. Pease, *Proc. Roy. Soc. (London)* **A220**, 397 (1953); **A230**, 359 (1955).

¹⁶ W. J. L. Buyers, R. A. Cowley, G. L. Paul, and W. Cochran, in *Proceedings of the IAEA Symposium on Inelastic Neutron Scattering*, 1968 (to be published).

¹⁷ Recent ultrasonic (Ref. 9) and Brillouin scattering data

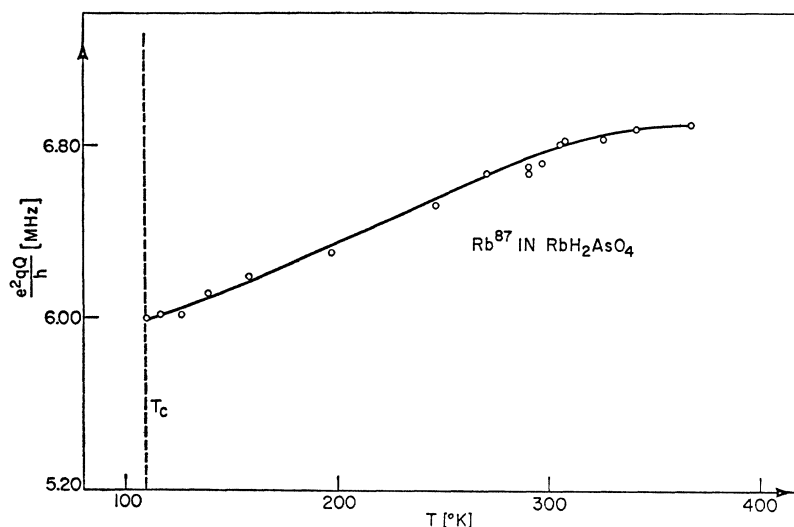


FIG. 2. Temperature dependence of the Rb^{87} quadrupole coupling constant in the paraelectric phase.

paraelectric phase, all Rb nuclei are physically equivalent according to x-ray and neutron diffraction data^{14,15} and lie on inversion centers on the tetrad axes. The existence of the fourfold rotation axis thus requires $\eta=0$, and the $Z(c)$ direction, which is parallel to this axis, must be a principal axis of the EFG tensor.

The shift is nearly temperature-independent between 340 and 380°K and then—contrary to what is usually found—decreases with decreasing temperature down to the Curie point at 110°K. From the measured shifts $\Delta\nu_{1/2}$, we deduced the T dependence of the Rb^{87} quadrupole coupling constant e^2qQ/h , using both second-order perturbation theory,¹⁹

$$\Delta\nu_{1/2}^{(2)} = (-\nu_Q^2/16\nu_L)(a - \frac{3}{4})(1 - \mu^2)(9\mu^2 - 1), \quad (1)$$

$$a = I(I+1), \quad \mu = \cos\theta, \quad \nu_Q = e^2qQ/2h,$$

as well as the exact solutions²⁰ of the secular determinant, which for our case, where $\theta=90^\circ$, reduces to

$$T^2 \pm T - \frac{3}{4}(1 \pm 2\lambda + 3\lambda^2) = 0, \quad (2)$$

with $T = E_m/(\mu H/I)$ and $\lambda = e^2qQ/4\mu H_0$. Here all symbols have their usual significance.^{19,20}

The two approaches gave essentially identical results for e^2qQ/h . The temperature dependence of this quantity is presented in Fig. 2.

At the Curie point, the $\text{Rb}^{87} \frac{1}{2} \rightarrow -\frac{1}{2}$ line splits into two components A and B , and there is a sharp change in the T dependence of the shift (Fig. 1) which reflects the T dependence of the spontaneous polarization.²¹ For the Z rotation, each component is, in addition, split into two components because of domain effects, so that we get four lines: A , A' , B , and B' (Fig. 3). No line

broadening was observed on passing through the Curie point for $\theta_Z=0$.

Because of the lowering of the crystal symmetry from tetragonal $I\bar{4}2d$ (or, alternatively, $F\bar{4}d2$) to orthorhombic $Fdd2$ and the resulting transformation of the fourfold axis parallel to c into a twofold axis, the EFG tensor is no longer axially symmetric in the ferroelectric phase. The c axis is, however, still a principal axis of the field gradient, and a single rotation about this known axis is sufficient to determine the eigenvalues and the orientation of the principal axes of the EFG tensor at the Rb sites. The results (obtained by the method of Volkoff¹⁹) are summarized in Table I. There are now two physically nonequivalent Rb sites A and B in the unit cell, the EFG tensors of which are related by a 90° rotation around the $Z(c)$ axis. The signals from the oppositely polarized domains differ in the sign of the off-diagonal component V_{XY} . The quadrupole coupling constant is significantly lower ($e^2qQ/h = 5.76 \pm 0.06$ MHz) than in the paraelectric phase, and the asymmetry parameter is quite large: $\eta = (V_{xx} - V_{yy})/V_{zz} = 0.85 \pm 0.03$. The second and third largest principal axes of the A - and B -site Rb^{87} EFG tensor, V_{yy} and V_{xx} , make an angle of $\varphi = \pm 2^\circ 30' \pm 25'$, respectively, with the tetragonal $Y(b)$ and $X(a)$ axes and are, of course, perpendicular to the $Z(c)$ axis, which is the direction of the major principal axis, corresponding to V_{zz} .

The application of an electric field parallel to the $Z(c)$ axis removes the domain splitting.

Polarization-reversal results in a change in the environment of the Rb nuclei and in a transformation of $A \rightleftharpoons B'$ and $B \rightleftharpoons A'$, where primed and unprimed symbols refer to oppositely polarized domains.

DISCUSSION

The above data throw some light on (i) structural considerations concerning the location of the Rb atom

¹⁹ G. M. Volkoff, Can. J. Phys. **31**, 820 (1953); M. H. Cohen and F. Reif, Solid State Phys. **5**, 321 (1957).

²⁰ P. M. Parker, J. Chem. Phys. **24**, 1096 (1957).

²¹ In view of the limited amount of data in the ferroelectric phase, no reliable quantitative conclusions can be made on the value of n in the relation $\Delta\nu_{1/2}^{(2)} \propto P^n$.

in the paraelectric phase, (ii) the effect of the ferroelectric transition on the EFG tensor at the Rb site, and (iii) the nature of the thermal motion and the proton-lattice coupling in the paraelectric phase.

(i) *Structural considerations.* According to x-ray and neutron diffraction data,^{14,15} the Rb and As atoms lie in the paraelectric phase on inversion centers on the tetrad axes. Recently, however, it has been pointed out¹³ that this might not be necessarily so, and that the symmetry requirements concerning the Rb position might be satisfied only in a statistical sense, i.e., the Rb atoms might be statically or dynamically disordered between two rather close ($\Delta l \sim 0.1 \text{ \AA}$) equilibrium sites symmetrically placed about the inversion center along the Z axis. If this would be true, the transition to the ferroelectric phase would be an order-disorder transformation insofar as the Rb^+ ions are concerned and not a displacive one, as has been usually assumed. The Rb behavior would be thus similar to the proton behavior for which the order-disorder nature is well established.

Static disorder can be immediately ruled out by the present data, since in this case the environment of the Rb atom would be subject to unsymmetrically acting short-range forces resulting in a local polarization and the appearance of two different Rb EFG tensors instead of the one observed. The dynamical order-disorder model cannot be rejected on the basis of the multiplicity of the Rb lines. The fact (Table I) that the EFG tensor in the paraelectric phase is roughly equal to the average over the two ferroelectric EFG tensors is also consistent with this model. Similarly, one can account for the absence of "exchange" broadening near T_c simply by requiring that the "exchange" frequency be still larger than the quadrupole splittings when the ferroelectric transition takes place. However, when one tries to account for some finer details such as the T dependence of the quadrupole coupling constant [see (iii)], one runs into difficulties and has to introduce a gradual change of the potential field with T which wipes out a clear-cut distinction between a displacive and an order-disorder transition for the Rb ion.

In the following, we shall therefore assume that in the paraelectric phase the Rb ions move around their symmetry-fixed positions on the Z axis without specifying for the moment the nature of this motion.

(ii) *Effect of ferroelectric transition on EFG tensor at Rb sites.* The influence of the ferroelectric transition on the Rb^{87} EFG tensor can be qualitatively, though not quantitatively, understood on the basis of the point-charge model and the known changes in the crystal structure at T_c . As mentioned above, the Rb ions are in the paraelectric phase centered at the inversion centers on the fourfold axes and are surrounded by eight electronically equivalent O neighbors, which may be grouped into two interpenetrating tetrahedra with nearly equal Rb-O distances. The protons are dynamically disordered, between the two equilibrium sites in the H bonds. Below T_c , the framework of the oxygen atoms

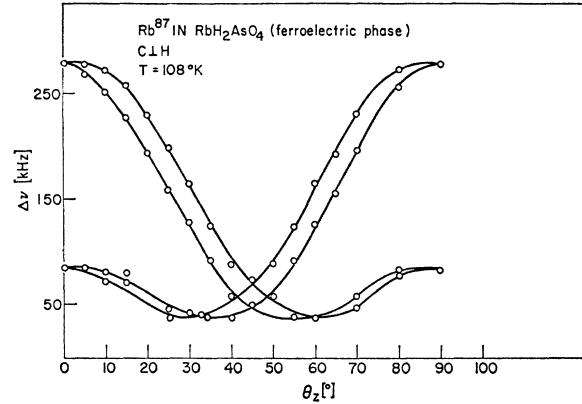


FIG. 3. Angular dependence of the shift of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ Rb^{87} NMR transition in the ferroelectric phase for a rotation about the C axis in an unpoled crystal. Each A - or B -site line is split into two components because of domain effects.

changes very little. The Rb atoms move up in the Z direction by approximately 0.06 \AA , the As atoms move down the Z axis by about 0.05 \AA (where "up" and "down" are here specified by an arbitrary choice of sense of the Z axis), and the protons order so that each AsO_4 group has two O-H groups for its upper corners and two O atoms for its lower corners. The principal effect of the proton ordering will be a change in the effective charge around the oxygens (as seen by the Rb atom) and a resulting division of the oxygen framework into two electronically inequivalent sets (As-O and As-OH) with slightly different Rb-O distances. The proton ordering thus destroys the axial symmetry of the field gradient and is responsible for the rather large value of $\eta = (V_{xx} - V_{yy})/V_{zz}$. The displacement of the Rb atom along the $Z(c)$ axis with respect to the now electrically nonequivalent oxygen framework, on the other hand, mainly influences V_{zz} , i.e., the quadrupole coupling constant. The observed direction of the changes on going to the ferroelectric phase, i.e., the decrease in V_{zz} and V_{xx} and the increase in V_{yy} , agrees with the predictions of the point-charge model calculations, but a good quantitative agreement could not be obtained. A more thorough treatment of this problem with the inclusion of the induced electric dipole contributions to the field gradient has been postponed until EFG tensors at the cation and anion sites in several isomorphous crystals are determined.

TABLE I. Rb^{87} quadrupole coupling tensor components (MHz) in the crystal-fixed (tetragonal) $X(a)$, $Y(b)$, $Z(c)$ system of RbH_2AsO_4 . Primed and unprimed symbols refer to oppositely polarized domains.

T ($^{\circ}\text{K}$)		e^2QV_{zz}/h	e^2QV_{yy}/h	e^2QV_{xx}/h	e^2QV_{xy}/h
108	A	5.76 ± 0.06	-5.34 ± 0.06	-0.42 ± 0.06	0.21 ± 0.03
	B	5.76 ± 0.06	-0.42 ± 0.06	-5.34 ± 0.06	0.21 ± 0.03
	B'	5.76 ± 0.06	-0.42 ± 0.06	-5.34 ± 0.06	-0.21 ± 0.03
	A'	5.76 ± 0.06	-5.34 ± 0.06	-0.42 ± 0.06	-0.21 ± 0.03
370	$A = B$	6.90 ± 0.06	-3.45 ± 0.06	-3.45 ± 0.06	0

For now, the field-gradient data at the Rb site can be compared only with the K^{39} data recently obtained²² at room temperature and at 77°K in KH_2PO_4 by a double-resonance technique. The effect of the ferroelectric transition on the cation EFG tensor is qualitatively similar to the one in RbH_2AsO_4 . On going to the ferroelectric phase, the asymmetry parameter increases from zero to $\eta \approx 0.7$, and the K^{39} quadrupole coupling constant decreases from 1.68 to 1.48 MHz. Both the change in η and the relative change in the quadrupole coupling constant are thus slightly smaller than in RbH_2AsO_4 . The ratio of the two quadrupole coupling constants in the ferroelectric phase is

$$(e^2qQ)_{Rb^{87}}/(e^2qQ)_{K^{39}} = 3.9. \quad (3)$$

Since the Rb^{87} quadrupole moment is twice as large as the K^{39} quadrupole moment, the ratio of the field gradients in the Z direction at the two-cation nuclei is

$$\frac{q_{Rb}}{q_{K^{39}}} = \frac{(1+\gamma_\infty)_{Rb}q_{latt}(Rb)}{(1+\gamma_\infty)_K q_{latt}(K)} = 1.95. \quad (4)$$

According to the calculations of Sternheimer as cited in Ref. 19, the values of the two antishielding factors γ_∞ are 18.2 for K^+ and 70.7 for Rb^+ . The lattice contribution to the field gradient q_{latt} at the cation site in KH_2PO_4 thus seems to be (below T_c) twice as large as in RbH_2AsO_4 :

$$q_{latt}(Rb)/q_{latt}(K) = 0.52. \quad (5)$$

The same result for $q_{latt}(Rb)/q_{latt}(K)$ is obtained if the room-temperature quadrupole coupling constants are compared. Qualitatively this is exactly what is expected, since the unit-cell dimensions in KH_2PO_4 are smaller than in RbH_2AsO_4 . Further work is needed, however, to see whether the whole difference can be described only in terms of the changes in the lattice constants (KH_2PO_4 : $a = 7.453 \text{ \AA}$, $C = 6.975 \text{ \AA}$; RbH_2AsO_4 : $a = 7.793 \text{ \AA}$, $C = 7.467 \text{ \AA}$) and interionic distances, or whether a small part of it might be due to the fact that the true value of the K^+ antishielding factor is somewhat larger than cited in the literature.

(iii) *Temperature dependence.* The anomalous temperature dependence of the Rb^{87} quadrupole coupling constant in the paraelectric phase is of particular importance for the discrimination between the possible models of atomic motion in the damped ferroelectric mode or (using another language) in the order-disorder polarization fluctuations mentioned in the Introduction. Before attempting such an analysis, however, one must carefully evaluate all other factors influencing the temperature behavior of the EFG tensor.

The changes in the quadrupole-perturbed NMR frequencies with temperature are generally the result of both thermal expansion of the lattice parameters and

²² M. Kunitomo, T. Terao, Y. Tsutsumi, and T. Hashi, J. Phys. Soc. Japan **22**, 945 (1967); **24**, 429 (1968).

the thermal motion. Kushida, Benedek, and Bloembergen²³ proposed the following phenomenological equation²⁴ for the temperature dependence of the quadrupole resonance frequencies at atmospheric pressure:

$$\frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \frac{1}{v} \left[\frac{\partial v}{\partial q} \cdot \frac{\partial q}{\partial V} \left(\frac{\partial V}{\partial T} \right)_P + \frac{\partial v}{\partial \eta} \cdot \frac{\partial \eta}{\partial V} \left(\frac{\partial V}{\partial T} \right)_P + \sum_i \frac{\partial v}{\partial \xi_i} \left(\frac{\partial \xi_i}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial v}{\partial T} \right)_V \right], \quad (6)$$

where

$$\left(\frac{\partial v}{\partial T} \right)_V = \sum_i \frac{\partial v}{\partial \xi_i} \left(\frac{\partial \xi_i}{\partial T} \right)_V, \quad (7)$$

with $v = \nu_q$ and with ξ_i designating the amplitudes of the normal modes of vibration of the crystal.

The first term,

$$\frac{1}{v} \frac{\partial v}{\partial q} \cdot \frac{\partial q}{\partial V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{q} \frac{\partial q}{\partial V} \left(\frac{\partial V}{\partial T} \right)_P,$$

measures the effect on q of the change in the spatial distribution of the electric charges due to thermal expansion of the lattice. Expressing the volume dependence of the quadrupole coupling constant as $q \propto V^n$, and denoting the thermal expansion coefficient by $\alpha = 1/V \cdot (\partial V/\partial T)_P$, one gets an estimate for the temperature variation of q due to volume expansion as

$$\frac{1}{q} \left(\frac{\partial q}{\partial V} \right) \left(\frac{\partial V}{\partial T} \right)_P = n \cdot \alpha. \quad (8)$$

For ionic bonding, q depends on the interatomic distances as $1/R^3$, and $n = -1$. As $\alpha = (7.6 \times 10^{-5})/^\circ C$ for RbH_2AsO_4 ,²⁵ Eq. (8) yields $n \cdot \alpha = (-0.76 \times 10^{-4})/^\circ C$, whereas the experimental value of the relative change in the quadrupole coupling constant with temperature is $1/q \cdot (\partial q/\partial T)_P = (+0.7 \times 10^{-3})/^\circ C$ in the region 110–310°K.

The effect of thermal expansion thus cannot explain the experimental data. It is by an order of magnitude too small and has the wrong sign. Any covalent character of the Rb bonding would decrease the absolute of n , but could not close the gap between the predicted and observed temperature variation of q .

The asymmetry parameter is zero in the paraelectric phase and thermal expansion will not change the axial symmetry. Therefore, the second term in Eq. (6), $(\partial v/\partial \eta) \cdot (\partial \eta/\partial V) (\partial V/\partial T)_P$, is zero.

There is very little information available on the third term, $(\partial v/\partial \xi) (\partial \xi/\partial V)_T \cdot (\partial V/\partial T)_P$, which contains the

²³ T. Kushida, G. B. Benedek, and N. Bloembergen, Phys. Rev. **104**, 1364 (1956).

²⁴ Equation (6) and the following discussion of the thermal-expansion effects are strictly valid only for an isotropic crystal. However, the treatment can be easily extended to the anisotropic case, and all conclusions based on Eq. (6) remain valid.

²⁵ W. R. Cook, Jr., J. Appl. Phys. **38**, 1637 (1967).

volume dependence of the vibration amplitudes. For a quasiharmonic "stable" crystal, $(\partial\xi/\partial V)_T > 0$, $(\partial V/\partial T)_P > 0$, $(\partial\nu/\partial\xi) < 0$, so that the predicted temperature effect has the wrong sign. The measured pressure dependence of the vibrational spectra of KH_2PO_4 in the paraelectric phase²⁶ above 80 cm^{-1} indeed showed that $d\omega_i/dP \geq 0$, so that $d\xi_i/dV \geq 0$. The largest contribution to this term, however, is expected to arise from the very-low-frequency ferroelectric mode, the pressure dependence of which has not yet been directly studied. The observed decrease of the Curie temperature of KH_2PO_4 with increasing pressure,²⁷ on the other hand, suggests that the frequency of this mode increases with increasing pressure, so that the above conclusion remains valid and the third term in Eq. (6) can be as well dismissed as a cause for the observed temperature dependence.

We are thus lead to the conclusion that the anomalous temperature dependence of the Rb quadrupole coupling constant in the paraelectric phase, $(1/q)(\partial q/\partial T)_P \approx (+0.7 \times 10^{-3})/^\circ\text{C}$, cannot be understood by the first three terms in Eq. (6) and therefore should *per exclusionem* be describable by the last term,

$$\frac{1}{v} \sum_i \frac{\partial v}{\partial \xi_i} \left(\frac{\partial \xi_i}{\partial T} \right)_V,$$

representing the effect of the variation of the amplitude of atomic motion with temperature at constant volume.

Lattice vibrations or critical fluctuations cause the components of the EFG tensor to fluctuate with time around some equilibrium values at frequencies which are normally much higher than the quadrupole energy-level separations.

The nuclear quadrupole moments thus "see" only the time-averaged values of the EFG tensor: $(V_{ij})_{\text{obs}} = \langle V_{ij}(t) \rangle_{\text{av}}$. These averages depend on temperature both via the change in the population of the excited states and via a possible change in the lattice spectrum if the crystal is not "stable."

Expanding the time average of q in terms of normal modes of vibration,²³ one finds the relation between the effective quadrupole coupling constant $\langle q \rangle$ and the mean-square vibration amplitudes ξ_i^2 of the i th normal mode as

$$\langle q \rangle \approx q_0 \left(1 - \frac{3}{2} \sum_i \frac{1}{2} A_i \xi_i^2 \right), \quad (9)$$

where, of course, $A_i = -\frac{2}{3} \delta_{ii}$, with $q_0 \delta_{ii}$ being the second-order expansion coefficient of $\langle q \rangle$ in terms of ξ_i , and q_0 is the value of \bar{q} in a rigid lattice. For the low-frequency modes ($\hbar\omega \leq kT$), which have the most pronounced effect on \bar{q} in particular, one gets

$$\frac{1}{2} \xi_i^2 = kT/\omega_i^2, \quad (10)$$

so that for a "stable" crystal [$\omega_i \neq \omega_i(T)$], ξ_i^2 linearly

decreases with decreasing temperature. A point-charge model calculation has, however, shown that the observed decrease in q with decreasing temperature can be explained if $\langle \xi_i^2 \rangle$ increases and not decreases with decreasing temperature. The increase in ξ_i^2 with decreasing temperature can easily be understood qualitatively with the help of the fluctuation-dissipation theorem. If ξ_i is the normal coordinate proportional to the Z component of the ionic polarization, then one obtains in the classical limit with the help of the sum rule

$$\langle \xi_i^2 \rangle = \text{const} T \cdot \epsilon_{\text{ion},Z}(0), \quad (11a)$$

where $\epsilon_{\text{ion},Z}(0)$ is the ionic contribution to the static dielectric constant in the Z direction, which is known to increase on approaching the Curie point. An equivalent way of dealing with this problem is to drop the assumption that the lattice is stable in the paraelectric phase and to allow for a decrease in the frequency ω_i of one of the lattice modes when cooling the crystal towards the Curie point. The relative temperature independence of the quadrupole coupling constant in the region 340–370°K fits very well into this model, and is explained as the result of a decrease in the amplitude of the unstable mode and a near cancellation of the positive contribution to $(1/q)(\partial q/\partial T)$ due to the unstable mode and of the negative contribution due to the "stable" modes and thermal expansion. (Since the averaging effect of the stable modes is relatively small, one can take the high T value of q as q_0 in discussing the effect of the unstable mode.) If should be stressed, however, that a simple undamped ferroelectric mode, which depends on temperature as

$$\omega_-^2 = \kappa(T - T_0), \quad (11b)$$

with $T_0 = T_c$ being the Curie temperature, cannot quantitatively account for the observed nearly linear decrease in q with decreasing temperature, without any significant change in slope in the vicinity of T_c . If, however, the mode is strongly damped and if the ferroelectric transition occurs before ω_-^2 becomes zero, so that the difference between the Curie temperature T_c and T_0 is at least 10°K , the experimental q -versus- T curve can be approximately reproduced.

Another practically equivalent way of explaining the experimental results is to assume the existence of rapid order-disorder polarization fluctuations, the mean-square amplitude of which increases as one approaches the Curie point. In such a picture,

$$\bar{q} = \sum_i q_i w_i, \quad (11c)$$

where w_i is the weight of the state in which the quadrupole coupling constant equals q_i , and $\sum_i w_i = 1$.

Various fluctuation models are possible. The simplest is the "pure" rigid-lattice order-disorder model, which assumes not only that there is a symmetrical double-minimum potential field for the collective proton motion—which seems now to be well established—but

²⁶ R. Blinc, C. Postmus, and J. R. Ferraro (unpublished).

²⁷ H. Umehayashi, B. C. Frazer, and G. Shirane, *Solid State Commun.* **5**, 591 (1967).

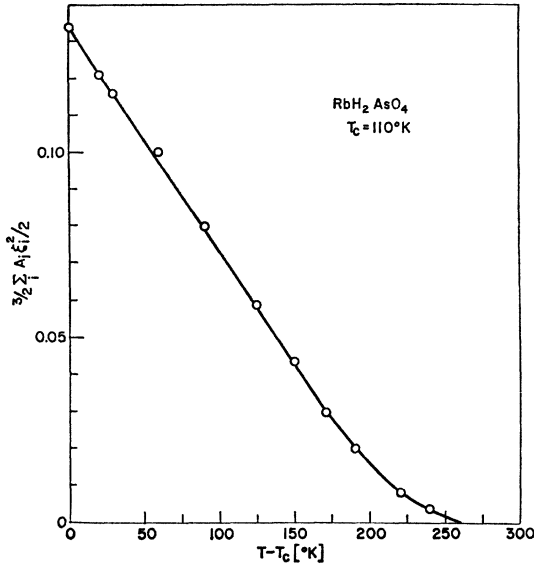


FIG. 4. Temperature variation of the square of the weighted amplitude of the ferroelectric "normal" mode in RbH_2AsO_4 according to Eq. (9). The quantity q_0 was arbitrarily taken as the value of q at 380°K , so that $\frac{3}{2} \sum_i A_i \xi_i^2$ is counted relative to its value at 380°K . The weighting factor A_i represents the efficiency of a given normal-mode displacement in changing the Rb^{87} quadrupole coupling constant.

also that the Rb ions move between two equivalent sites along the Z axis in the "rigid" framework of the oxygen atoms. In such a case, a polarization fluctuation would result in a change of $A \rightarrow B'$ and $B \rightarrow A'$ (Table I), and the paraelectric EFG tensor should be exactly equal to the average of the two ferroelectric Rb EFG tensors:

$$(V_{XX})_{\text{para}} = \frac{1}{2}[(V_{XX})_A + (V_{XX})_{B'}] = (V_{YY})_{\text{para}}, \quad (12a)$$

$$(V_{YY})_{\text{para}} = \frac{1}{2}[(V_{YY})_A + (V_{YY})_{B'}] = (V_{XX})_{\text{para}}, \quad (12b)$$

$$(V_{ZZ})_{\text{para}} = \frac{1}{2}[(V_{ZZ})_A + (V_{ZZ})_{B'}], \quad (12c)$$

$$(V_{XY})_{\text{para}} = \frac{1}{2}[(V_{YX})_A + (V_{XY})_{B'}] = 0. \quad (12d)$$

Whereas Eqs. (12a)–(12d) are relatively close to the experimental situation, it should be remembered that such an averaging ($A \rightarrow B'$, $A' \rightarrow B$) is not specific for the above model, but follows from any order-disorder or "unstable mode" approach which involves a collective flipping of the protons between the two equilibrium sites in the H bonds. Since $(V_{ZZ})_A = (V_{ZZ})_B$, polarization fluctuations in the above model do not produce any temperature dependence of the quadrupole coupling constant, and thus by itself, cannot explain the experimental data. In order to explain the observed temperature dependence of the quadrupole coupling constant, one must either allow for a gradual change of the Rb potential field with temperature—bringing us back to a proton-cation quasispin-wave unstable-mode model—or replace the simple two-minima potential field for Rb motion with another anharmonic field, in which the Rb nucleus spends part of its time in the paraelectric phase

at the inversion center and part of its time at an off-center position.

In such a case one may assume that the unit-cell structure rapidly fluctuates between the paraelectric ground state (w_0) and two metastable ferroelectric states (w_{fer}) of opposite but fixed polarity $\delta P = \pm P$, so that

$$\bar{q} = w_0 q_0 + 2w_{\text{fer}} q_{\text{fer}} \quad (13)$$

and $\langle P \rangle = 0$, $\langle \delta P^2 \rangle = 2w_{\text{fer}} P^2$.

Within this model one finds (Fig. 4) from the experimental data that the weight of the paraelectric state w_0 decreases nearly linearly from $\sim 100\%$ at 380°K to 18% immediately above the Curie point. Not too much significance, however, should be attached to numbers derived from such an oversimplified model. The observed T dependence of q can, according to this model, be explained if the change in the appropriate free-energy function ΔG associated with the polarization fluctuation δP is less than kT . In such a case,

$$w_{\text{fer}}(\delta P) \propto e^{-\Delta G/kT} \approx 1 - \Delta G/kT \quad (14)$$

and

$$w_0 \propto \Delta G/kT. \quad (15)$$

Neglecting for the sake of simplicity elastic and piezoelectric terms, which in the present case only renormalize the transition temperature, one finds that

$$\Delta G = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \dots, \quad (16)$$

with

$$a = a'(T - T_0). \quad (17)$$

Since b is approximately T -independent, one obtains for the T dependence of w_0 and \bar{q}

$$\bar{q} = q_{\text{fer}} + (q_0 - q_{\text{fer}})w_0 = \text{const} + K(T - T_0)/T + \dots \quad (18)$$

Equation (18)—as in the "damped unstable mode" picture—qualitatively reproduces the observed q -versus- T curve, but runs into difficulties when trying to account for the nearly constant slope. In view of the simplifications made [one of which is the assumption that $\delta P = \pm P \neq f(T)$], not more than a qualitative agreement could be expected anyway.

If the frequency of the fluctuations is still high compared to the quadrupole splitting in question immediately above the Curie point, only one line will be seen all the way down to the ferroelectric phase. If, however, the fluctuations become too slow, three lines should appear. The absence of any broadening of the $\frac{1}{2} \rightarrow -\frac{1}{2}$ line at $\theta_z = 0$ seems to favor the former possibility.

In addition to demonstrating the existence of an overdamped unstable mode, or (what nearly amounts to the same thing) the existence of order-disorder polarization fluctuations, the Rb quadrupole coupling data as well throw some light on the nature of the ionic motion in this mode.

Point-charge model calculations show, namely, that a mode in which in the paraelectric phase the Rb

atoms are fixed at the inversion centers and the collective proton modes (or polarization fluctuations) rapidly flip the hydrogens between the two equilibrium sites (in such a way that the Slater rules are always obeyed) can indeed account for the experimental fact that the paraelectric EFG tensor is nearly, though not exactly, equal to the average of the two ferroelectric EFG tensors. Such a "rigid cation" model, however, cannot account for the observed T dependence of the EFG tensor and particularly of V_{zz} , in the paraelectric phase. This is still true if one allows for Rb motion along the Z axis as long as the frequency of this motion is much slower than the hydrogen motion, so that the Rb "sees" an averaged, effectively axially symmetric field with "half" a hydrogen attached to each of the eight surrounding oxygens. It is only when the frequencies of the Rb and the proton motion become of comparable magnitude (so that it is the instantaneous asymmetric proton arrangement which the Rb "sees" during its motion along the Z axis) that one finds a T dependence of the Rb quadrupole coupling constant and a decrease of V_{zz} with an increasing amplitude of Rb motion or (what amounts to the same thing) decreasing frequency. As long as the frequency of this motion is larger than the quadrupole energy-level splitting in the ferroelectric phase, one observes in NMR an effective EFG tensor which represents an average over the above-mentioned collective atomic fluctuations. This effective EFG tensor is axially symmetric and depends on temperature in a way described by Eqs. (18) or (10), with $\omega_i = \omega_i(T)$.

The present data thus support the first of the two possible models of proton-lattice coupling mentioned in the Introduction. It seems that at high temperatures (above 340°K) the frequency of the proton motion is higher than the frequency of the Rb motion, so that the Rb EFG tensor is nearly T -independent. As the T gets lower, the frequencies become comparable, so that a crossover of the phonon branches can occur and the hydrogen and Rb nuclei move in phase, resulting in an increase in the vibrational amplitude and a strong decrease in the Rb quadrupole coupling constant with decreasing temperature. In the ferroelectric phase, this motion freezes in and one sees two different Rb EFG tensors in a given domain. One may thus say that the

Rb EFG data support the statement that the structure of the ordered phase corresponds to a normal mode of the disordered phase in the region 110–340°K. Above 340°K, the proton system and the lattice seem to be effectively decoupled as a result of a large difference in the motional frequencies.

Since this model requires only a modest increase in the vibrational amplitude of Rb along the Z axis on approaching the Curie point, it does not necessarily contradict the neutron diffraction data,¹⁵ which show an over-all decrease in the cation mean-square displacement averaged over all normal modes.

The question of the role of the anion (i.e., the As ion) in this normal mode still remains. Though point-charge model calculations are probably less appropriate in this case in view of the large covalency effects, it seems clear that, in Eq. (9), $A < 0$, so that an increase in the amplitude of the unstable mode ξ_i^2 results in an increase in the As quadrupole coupling constant. Thus, the published data¹⁸ and the data obtained in this laboratory, as well as the data kindly shown to us by Professor Bjorkstam, all indicate a strong increase in the vibrational amplitude of the As motion on approaching the Curie point, and demonstrate its taking part in the collective atomic fluctuations. It is interesting to observe that the absolute value of the relative slope $[(1/q) \cdot (dq/dT)]_{\text{As}}$ between 20 and -130°C is practically the same¹⁸ as the one for Rb. In the vicinity of the Curie point, however, there is a pronounced change in slope in the As case which is not found in the Rb data. It might well be that covalency effects, which should be much more important in the As case than in the Rb case, start to play a role. Another factor is that the relative changes in the As-O distances due to As motion are much greater than the changes in the Rb-O distances. This is also borne out by the fact that the relative change in the As quadrupole coupling constant at the Curie point is for two orders of magnitude larger¹⁸ than the corresponding change in the Rb case.

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