

to us by Stettler. Excellent discussions of the strength and frequencies of Jahn-Teller distortions have recently been written,<sup>5,35</sup> indicating the  $\text{Cr}^{3+}$  ground state is not effected directly and therefore does not give rise to this localized motion.

### V. CONCLUSIONS

Within the  $S' = \frac{3}{2}$  ground state of  $\text{Cr}^{3+}$  ions in cubic sites in  $\text{MgO}$  at any given temperature over the range 40–180 K, the recovery from pulsed saturation is accurately described by a single relaxation time constant. No explanation of this is offered by these data.

The  $\text{Cr}^{3+}$  relaxation time near 3 kG is accurately given by the function  $\text{csch}(537/T)$  at all values of  $T$  from 75 to 430 K. Every other relaxation function based on either of the two measured phonon spectra or on a single Einstein mode exhibits systematic deviations

from the observed values much larger than the random experimental uncertainty based on measured signal to noise and confirmed by the statistics of repeated recoveries at each  $T$ . The  $\text{csch}$  function suggests relaxation via localized modes having temperature-independent amplitudes such as might be possible in motions of the  $\text{CrO}_6$  complex.

With the high-temperature relaxation fitted, the expected harmonic Raman relaxation functions account for more than 50% of the observed relaxation only in the range between 30 and 40 K, temperatures corresponding to less than 10% of the energy of the transverse acoustic peak. Apparently motions localized around each  $\text{Cr}^{3+}$  ion dominate the ground-state relaxation.

### ACKNOWLEDGMENTS

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<sup>35</sup> F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum Press, Inc., New York, to be published). Ham's chapter may also be available as Report No. 68C246 from General Electric Research and Development Center, Schenectady, N. Y. (unpublished).

## $\text{Rb}^{87}$ and $\text{As}^{75}$ Quadrupolar Coupling in Ferroelectric $\text{RbH}_2\text{PO}_4$ and $\text{CsH}_2\text{AsO}_4$ †

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The quadrupole-induced shifts of the  $\text{Rb}^{87}$  and  $\text{As}^{75}$   $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  nuclear-magnetic-resonance transitions have been used to study the temperature variation of the electric field gradients at the ionic sites on approaching the ferroelectric Curie points. The shifts can only be explained in terms of collective atomic fluctuations in the paraelectric phase. A soft-lattice-mode model does not quantitatively describe the temperature dependence of the frequency shifts. A model which explicitly takes into account the protonic disorder accounts quantitatively for the arsenic data. No quantitative treatment that is in good agreement with the rubidium data has been found.

### INTRODUCTION

IT is well known that the ferroelectric transitions in  $\text{KH}_2\text{PO}_4$ -type crystals are accompanied by displacements of the K and P ions in the  $+$  and  $-z$  ( $c$ ) directions, respectively, which accounts for the larger part of the spontaneous polarization. But whereas the proton motion and proton ordering have been investigated in great detail, relatively little is known on a microscopic scale on the motion of the heavy ions in the vicinity of the Curie point. It was often taken for granted that the proton system and the lattice motion are effectively decoupled in the paraelectric state, and that the polar lattice displacements occur only after the

proton ordering takes place. It was only recently that this "rigid" lattice model has been questioned and the importance of the coupling between proton motion and the polar lattice distortions for  $T > T_C$  was pointed out.

This investigation was made in the hope of throwing some additional light on the nature of the proton-lattice coupling in  $\text{KH}_2\text{PO}_4$ -type crystals by studying the temperature variation of the local electric field gradient (EFG) tensors at the Rb and As sites in  $\text{RbH}_2\text{PO}_4$  and  $\text{CsH}_2\text{AsO}_4$ . Together with the available information on the EFG tensor at the  $\text{Cs}^{133}$  site, these data should provide a sensitive test of the various theoretical models proposed so far.

#### A. $\text{As}^{75}$

The quadrupole-induced shifts of the  $\frac{1}{2} \rightarrow -\frac{1}{2}$  magnetic resonance transition of  $\text{As}^{75}$  ( $I = \frac{3}{2}$ ) in  $\text{CsH}_2$ -

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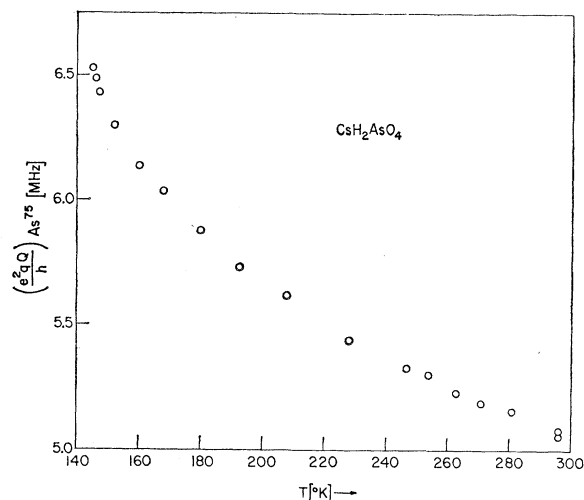


FIG. 1.  $\text{As}^{75}$  quadrupolar coupling constant  $e^2qQ/h$  versus temperature for  $\text{CsH}_2\text{AsO}_4$ .

$\text{AsO}_4$  have been measured as a function of temperature and crystal orientation at a frequency of 8.9193 MHz.

In the paraelectric phase the shift is independent of the angle of rotation around the  $Z$  axis, demonstrating axial symmetry ( $V_{xx} = V_{yy} = -\frac{1}{2}V_{zz}$ ) of the EFG tensor around this axis. The quadrupole coupling constants  $e^2qQ/h = eV_{zz}Q/h$  rapidly increase with decreasing temperature as  $T \rightarrow T_C$  as shown in Fig. 1.

The line shape is non-Lorentzian. The room-temperature linewidth is of the order of 10 kHz and varies with angular orientation. A significant line broadening occurs on approaching  $T_C$ , but no attempt was made to study this effect quantitatively.

The temperature variation of  $e^2qQ/h$  for  $T < T_C$  was studied in Refs. 1 and 2. We made only a rough check of the  $\text{As}^{75}$  spectrum at 77°K. There are two physically nonequivalent As sites in each domain in agreement with the structural data. The spectrum was found to be consistent with a quadrupole coupling constant,  $e^2qQ/h \approx 72$  MHz and an asymmetry parameter  $\eta = (V_{ii} - V_{jj})/V_{kk}$  (where  $V_{ii} \leq V_{jj} \leq V_{kk}$ ) of about 0.5, which agrees within the limits of experimental error with the values quoted in Refs. 1 and 2.

The application of an electric field, 3 kV/cm, parallel to the  $Z$  axis 10° above  $T_C$  resulted in a disappearance of the  $\text{As}^{75}$  signal. It took several months for the NMR signal to recover its original strength.

### B. $\text{Rb}^{87}$

The quadrupole-induced shifts of the  $\frac{1}{2} \rightarrow -\frac{1}{2}$  as well as  $\frac{1}{2} \rightarrow \frac{3}{2}$  NMR transitions of  $\text{Rb}^{87}$  ( $I = \frac{3}{2}$ ) in  $\text{RbH}_2\text{PO}_4$

have been measured as a function of temperature and crystal orientation at a frequency of  $\nu_L = 16.232$  MHz.

Similarly to the case of the  $\text{As}^{75}$  resonance the shifts are found to be independent of the angle of rotation around the  $Z$  axis for  $T > T_C$ . The EFG tensor in the paraelectric phase is thus axially symmetric and the  $Z$  axis is the largest principal axis of the field gradient. Contrary to the As case, however, the quadrupole coupling constant in the paraelectric phase decreases on approaching the Curie point as shown in Fig. 2.

Below the Curie point, the  $\text{Rb}^{87} \frac{1}{2} \rightarrow -\frac{1}{2}$  line splits into two components,  $A$  and  $B$ , demonstrating the existence of two physically nonequivalent Rb sites in the unit cell the EFG tensors of which are related by a 90° rotation around the  $z$  ( $c$ ) axis (Fig. 3). At  $-150^\circ\text{C}$ , the quadrupole coupling constant is significantly lower [ $e^2qQ/h = 9.06 \pm 0.45$  MHz] than in the paraelectric phase and the asymmetry parameter is quite large:  $\eta = 0.56 \pm 0.03$ . The second and third largest principal axes of the  $A$  and  $B$  site EFG tensors are nearly parallel to the tetragonal  $y$  ( $b$ ) and  $x$  ( $a$ ) axes, respectively, and are, of course, perpendicular to the  $z$  ( $c$ ) axis, which is still the direction of the largest principal axis of the EFG tensors.

Each  $A$  and  $B$  site line is, at some orientations, further split into two components due to domain effects. The data represented in Fig. 3 represent an average over these domain splittings.

Contrary to the As case, an applied electric field had no effect on the  $\text{Rb}^{87}$  spectrum in the paraelectric phase.

The line shape varied from crystal to crystal and was apparently determined by mechanical stresses. In a very good crystal, a modulation frequency-dependent doublet fine structure was seen at room temperature in the dispersion and indicating a Rb spin-lattice relaxation time of the order of  $10^{-1}$ – $10^{-2}$  sec.

## DISCUSSION

The experimental data obtained in this study show the same general behavior as the one recently found for the EFG tensors at the  $\text{As}^{75}$  sites in  $\text{KH}_2\text{AsO}_4$  and  $\text{RbH}_2\text{AsO}_4$ , and at the  $\text{K}^{39}$ ,  $\text{Rb}^{87}$ , and  $\text{Cs}^{133}$  sites in  $\text{KH}_2\text{PO}_4$ ,  $\text{RbH}_2\text{AsO}_4$ , and  $\text{CsH}_2\text{AsO}_4$ , respectively.<sup>1-5</sup> In all these cases the quadrupole coupling constant at the As site anomalously increases on approaching  $T_C$  from above, whereas it decreases at the K, the Rb, or Cs sites. In neither case can the temperature dependence be explained by the Bayer theory<sup>6</sup> or the refinements introduced by Kushida, Benedek, and Bloembergen.<sup>7</sup> It is clear that the anomalous temperature dependence of the

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<sup>3</sup> R. Blinc and M. Mali, Solid State Commun. (to be published).

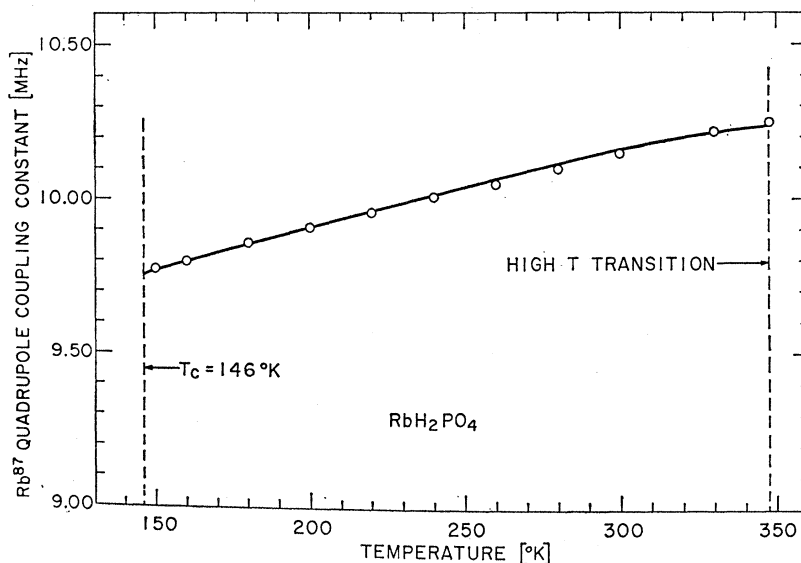
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<sup>1</sup> W. Beezhold and E. A. Uehling, Phys. Rev. 175, 624 (1968).

<sup>2</sup> A. P. Zhukov, I. S. Rez, V. I. Pakhomov, and G. K. Semin, Phys. Status Solidi 27, K129 (1968); J. L. Bjorkstam, Bull. Am. Phys. Soc. 1, 464 (1963); G. Cinader, Z. Zamir, and I. Pelah, Solid State Commun. 6, 435 (1968); R. Blinc and J. Bjorkstam, Phys. Rev. Letters 23, 788 (1969).

FIG. 2. Rb<sup>87</sup> quadrupole coupling constant versus temperature for RbH<sub>2</sub>PO<sub>4</sub>.



EFG reflects the collective atomic fluctuations responsible for the ferroelectric phase transition. A comparison between the experimental data and the predictions of the various theoretical models proposed so far might thus throw additional light on the nature of ferroelectricity in these crystals.

#### A. As Case

The EFG tensor at the As<sup>75</sup> sites in CsH<sub>2</sub>AsO<sub>4</sub> and isomorphous crystals is in view of the covalent nature of the As—O bonding mainly determined by the AsO<sub>4</sub> bond structure and only indirectly by the relative arrangement of the four hydrogens surrounding a given AsO<sub>4</sub> group. The frequency of modulation of the EFG tensor by the “soft” lattice mode or by the “dynamic” proton disorder which should be important in case of strong proton-lattice coupling is much larger than the instantaneous Larmor frequency of the nucleus. The positions of the As<sup>75</sup> lines are thus determined by an effective Hamiltonian

$$\mathcal{H}_0 = \mathcal{H}_M + \langle \mathcal{H}_Q \rangle_t, \quad (1)$$

which represents an average over the atomic position. Here  $\mathcal{H}_M = -\gamma \hbar \mathbf{H}_0 \cdot \mathbf{I}$  measures the Zeeman coupling of the As<sup>75</sup> nuclear spin to the external magnetic field  $\mathbf{H}_0$  and

$$\mathcal{H}_Q = \frac{e^2 V_{zz} Q}{4I(2I-1)} [3I_z^2 - I(I+1) + \frac{1}{2}\eta(I_+^2 + I_-^2)] \quad (2)$$

describes the interaction of the nuclear quadrupole moment with the EFG tensor  $V_{ij}$  at the As<sup>75</sup> site. It is expected that the time average  $\langle \mathcal{H}_Q \rangle_t$  is much smaller than the instantaneous value  $\mathcal{H}_Q$ , which can be measured below  $T_C$  as  $T \rightarrow 0$ . The fluctuating part of the

Hamiltonian

$$\mathcal{H}_1(t) = \mathcal{H} - \mathcal{H}_0 \approx \mathcal{H}_Q - \langle \mathcal{H}_Q \rangle_t \approx \mathcal{H}_Q, \quad (3)$$

on the other hand, determines the linewidth, which should be roughly of the order of  $\delta\nu = \hbar^{-2} \langle \mathcal{H}_Q^2 \rangle_t \tau$ , where  $\tau$  is the correlation time for atomic rearrangements in the H<sub>2</sub>AsO<sub>4</sub> group.

#### 1. Soft-Lattice-Mode Model

Let us first calculate the temperature dependence of the As<sup>75</sup> quadrupole coupling constant for the case that the “ferroelectric” mode which modulates  $\mathcal{H}_Q$  and  $V_{ij}$  is a “pure” lattice vibration, which “freezes in” below  $T_C$ . The atomic motion involved consists mainly of a vibration of As and Cs(Rb) ions in opposite directions along the  $z$  ( $c$ ) axis, which is as well the direction of the spontaneous polarization. Expanding  $V_{ij}$  in

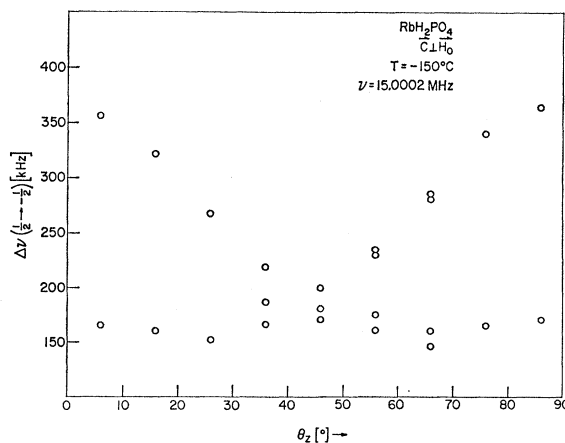


FIG. 3. Rotation pattern of second-order frequency shift of central line versus angle of rotation about the crystal  $c$  axis.

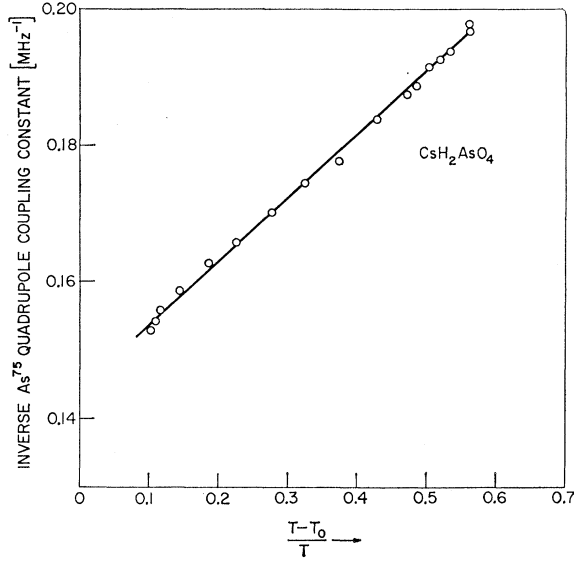


FIG. 4. Inverse  $\text{As}^{75}$  quadrupolar coupling constant versus  $(T-T_0)/T$ . Curie temperature is  $143^\circ\text{K}$ .

powers of the normal coordinate of the "ferroelectric" mode  $\xi(t)$ ,

$$V_{ij} = A_{ij} + B_{ij}\xi + C_{ij}\xi^2 + \dots, \quad (4)$$

and performing a time average, one finds that in the paraelectric phase

$$\langle V_{ij} \rangle_t \approx C_{ij} \langle \xi^2 \rangle_t \quad (5)$$

as the time average of  $\xi$  vanishes and  $A_{ij}$  is zero for a perfect tetrahedron. Below  $T_C$ , on the other hand, the time average of  $\xi$  is different from zero, and

$$\langle V_{ij} \rangle_t \approx B_{ij} \langle \xi \rangle_t. \quad (6)$$

Using the fluctuation-dissipation theorem

$$\xi^2 = \text{const} \times T \epsilon_{\text{ion}, z}^{(0)}, \quad (7)$$

where  $\epsilon_{\text{ion}, z}^{(0)}$  is the same contribution to the static dielectric constant in the direction of the ferroelectric axis, one gets the temperature dependence of  $e^2 q Q / h$  for  $T > T_C$  as

$$e^2 q Q / h = K T / (T - T_C), \quad (8)$$

where  $T_C$  is the Curie temperature at which  $\epsilon(0) \rightarrow \infty$ .

This result disagrees with the experimental data. As it can be seen from Fig. 4, the inverse quadrupole coupling constant is indeed linear in  $(T-T_0)/T$ , but  $T_0$  is not at all identical with  $T_C$ . For  $\text{CsH}_2\text{AsO}_4$ ,  $T_0 = 0.43 T_C$ , in obvious contradiction with Eq. (8).

The simple pure soft-lattice-mode model thus can *not* account for the temperature dependence of the EFG at the  $\text{As}^{75}$  sites. Alternative possibilities are:

(i) The proton-lattice coupling is very strong for  $T > T_C$  and it is the proton dynamics which determines

the temperature dependence of the EFG tensor at the As site.

(ii) The  $T$  dependence of the field gradient is governed by a lattice mode which does *not* condense at  $T_C$  but would condense at  $T_0 = 0.43 T_C$  in the absence of the ferroelectric transition at  $T_C$ .

Possibility (ii) can not be eliminated at present. Since, however, no evidence for such a mode has been found in the Raman or Brillouin scattering spectrum of  $\text{KH}_2\text{PO}_4$ , we shall discuss only alternative (i).

## 2. Proton-Disorder Model

In case of strong proton-lattice coupling it is the dynamic disorder of the hydrogens, moving between two equilibrium sites in the O—H—O bonds, which modulates  $V_{ij}$ . Neglecting for sake of simplicity tunneling effects and replacing the time average by an ensemble average, we find

$$V_{ij} = \sum_{l=1}^6 \delta_l (V_{ij}^{(l)}), \quad (9)$$

where the  $\delta_l$  are the weights of the six "allowed" Slater  $\text{H}_2\text{AsO}_4$  configurations and  $V_{ij}^{(l)}$  are the corresponding EFG tensors. The configurations 1 and 2 correspond to the case where both hydrogens are at the "top" and at the "bottom" oxygens, respectively—if one looks along the  $c$  axis—resulting in a nonzero electric dipole moment of the  $\text{H}_2\text{AsO}_4$  group in the  $+z$  ( $c$ ) and  $-z$  ( $c$ ) directions, respectively. In the configurations 3, 4, 5, 6, on the other hand, one hydrogen is attached to the upper and one to the lower oxygen, so that the  $c$  component of the dipole moment of the  $\text{H}_2\text{AsO}_4$  group vanishes. In view of their much higher excitation energy, the "defect"  $\text{H}_3\text{AsO}_4$ , etc., configurations make a negligible contribution to  $\langle V_{ij} \rangle_t$ .

Since the configurations 1 and 2 are the ones found in the completely ordered ferroelectric state in the  $+$ , respectively, domains,  $V_{ij}^{(1,2)}$  should be proportional to the EFG tensors  $V_{ij}(\pm P)$  measured below  $T_C$ ,

$$V_{ij}^{(1,2)} = \kappa V_{ij}(\pm P), \quad (10)$$

with

$$\frac{eQV_{ij}}{h} (+P) = \begin{bmatrix} 75 & 0 & 0 \\ 0 & -56 & 0 \\ 0 & 0 & -19 \end{bmatrix} \text{ MHz}, \quad (11a)$$

$$\frac{eQV_{ij}}{h} (-P) = \begin{bmatrix} -56 & 0 & 0 \\ 0 & 75 & 0 \\ 0 & 0 & -19 \end{bmatrix} \text{ MHz}, \quad (11b)$$

where the smallest principal axis  $V_{zz}$  is parallel to the  $c$  axis and the two major principal axes ( $V_{xx}, V_{yy}$ ) are nearly parallel to the two  $\text{AsO}_4$  tetrahedral edges lying in the  $a, b$  plane. The proportionality factor  $\kappa$ , which is

assumed to be a scalar, measures the strength of the proton-lattice coupling. It would equal to one if the deformations of the AsO<sub>4</sub> group above  $T_C$  would be exactly the same as below  $T_C$  and would be close to zero if the proton rearrangements would have no effect on the AsO<sub>4</sub> bond structure.

Though the EFG tensors for the four nonpolar configurations 3,4,5,6, which should dominate in the ferroelectric domain walls, have not been directly measured, one can assume (in view of the proportionality of the As<sup>75</sup> EFG tensor to the induced As displacement from its average paraelectric site) that  $V_{ij}^{(1/2)} \gg V_{ij}^{(3,4,5,6)}$ . As  $\delta_1 = \delta_2$  for  $T > T_C$ , we thus get, in agreement with experiment, an axially symmetric EFG tensor in the paraelectric phase

$$\frac{eQ\langle V_{ij} \rangle_t}{h} = \frac{eQ}{h} \delta_1 (V_{ij}^{(1)} + V_{ij}^{(2)})$$

$$= \delta_1 \kappa \begin{bmatrix} 19 & 0 & 0 \\ 0 & 19 & 0 \\ 0 & 0 & -38 \end{bmatrix} \text{ MHz}, \quad (12)$$

where

$$\delta_{1,2} = \frac{\delta_0}{4} \frac{1 \pm p}{1 \mp p} e^{\epsilon/kT} \quad (13a)$$

and

$$\delta_0 = \left[ 1 + \frac{1}{2} e^{\epsilon/kT} \left( \frac{1+p^2}{1-p^2} \right) \right]^{-1}, \quad (13b)$$

with  $p = p/p_\infty$  standing for the reduced value of the spontaneous polarization and  $\epsilon = kT_C \ln 2$  being the Slater short-range energy parameter. It should be noted that at  $T = T_C$ ,  $\delta_1 = \delta_2 = \frac{1}{4}$ , so that

$$\kappa = \frac{(eQV_{zz}/h)T = T_C}{eQV_{zz}(\pm P)/2h} = 0.72, \quad (14)$$

which seems to be a rather reasonable value. This result seems to prove that the proton-lattice coupling is very strong and that the As nuclei as well as the protons take part in collective atomic fluctuations on approaching  $T_C$ .

A further test on the validity of this model is provided by the temperature dependence of  $e^2qQ/h$  which depends on just one parameter, the Slater short-range energy  $\epsilon$ . Expression (12) indeed reproduces the observed temperature dependence of  $e^2qQ/h$  with  $\epsilon/k = 120^\circ\text{K}$ . The theoretical value of  $\epsilon$  obtained from  $\epsilon = kT_C \ln 2$  equals  $99^\circ\text{K}$ . The agreement is rather good and provides additional support for the dynamic

proton order-disorder model of ferroelectricity in KH<sub>2</sub>PO<sub>4</sub>-type crystals.

It is interesting to note that by expanding  $\delta$ , in powers of  $T_C/T$  for  $T > T_C$ , Eq. (12) can be rewritten up to first-order terms as

$$e^2qQ/h = \kappa T / (T - 0.45T_C), \quad (15)$$

in striking agreement with the experimental data (Fig. 4) which show that  $T_0 = 0.43T_C$ .

It should be stressed, however, that though the present data show the essential correctness of the Slater order-disorder model no detailed information is obtained on the dynamics of the system. A possible dynamic description of the situation would be that the EFG changes at the As sites are determined by the fluctuations in the phonon coordinates of an optical mode which is coupled to an unstable quasispin wave proton mode. Because of proton-lattice coupling, the phonon coordinates follow the quasispin coordinates adiabatically. The ferroelectric transition occurs when the frequency of the coupled proton lattice mode approaches zero. This happens when the frequency of the proton quasispin wave mode is still high.

## B. Rb Case

In contrast to the As case the field gradient at the Rb site is primarily ionic in origin. Thus it depends on the distribution of the electric charges in the whole lattice and not only in the immediate neighborhood of the ion as in the As case. A quantitative estimate of the  $T$  dependence of the field gradient is thus much more difficult and contains more than one unknown parameter.

Two important points however, must be stressed. The first is that a combination of the point charge and the "pure" soft-lattice-mode model predict the wrong sign of the temperature dependence of the field gradient in the paraelectric phase. The second is that they predict an *increase* in  $e^2qQ/h$  on going to the ferroelectric phase, whereas experimentally a *decrease* is observed. This is true for the charge assignments made by Jona and Shirane<sup>8</sup> as well as Bacon and Pease.<sup>9</sup> It is only when the proton motion is included that a qualitative though not quantitative agreement with experiment seems to be possible. Both the Rb and As results thus demonstrate the importance of proton-lattice coupling and strongly support the idea that it is the proton system which triggers the ferroelectric transition in these types of crystals.

<sup>8</sup> F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962), p. 93.

<sup>9</sup> G. E. Bacon and R. S. Pease, Proc. Roy. Soc. (London) **A220**, 397 (1953); **A230**, 359 (1955).