where B is given in (2), and

$$G=\frac{2}{u}\{(w+u)\ln(1+w+u)-(w-u)\ln(1+w-u)-2u(1+\ln w)\}. \quad (11)$$

Replacement of V_c by $V_{\bar{c}-\bar{a}}$ in (9) gives also the expression corresponding to the exchange correlation energy presented by Macke.[10] It should be noticed that in (10) an approximation introduced by Macke is included [reference 1, Eq. (24)].

3. SIMPLIFIED SELF-CONSISTENT FIELD EQUATIONS

If we include (3) and put $V_{\bar{c}}$ and $V_{\bar{c}-\bar{a}}$ into the Schrödinger equation, we obtain the self-consistent field equations developed by the correlation potentials:

$$\left\{H+U+A-e^2\cdot\frac{3}{2}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\{\sum_k \psi_k{}^*\psi_k\}^{\frac{1}{3}}\int_0^1 du\left[\cdots\right]\right.$$
$$\left.\times dw\frac{B(u,w)-G(u,w)}{4\pi^{5/3}3^{\frac{1}{3}}\{\sum_k \psi_k{}^*\psi_k\}^{\frac{1}{3}}+B(u,w)}\right\}\psi_i=E_i\psi_i, \quad (12)$$

where H, U, A, respectively, have conventional meaning of the Hamiltonian operator of the one-electron problem and the Coulomb and exchange operators of the given multielectron problem (Hartree-Fock operators), and where the brackets enclose the same integrals as in Eqs. (8) and (10). Three important consequences of (12) which were already a feature of the Hartree-Fock equations and their simplification given by Slater[11] hold: 1. The ψ_i functions may be presented in orthogonal form (one-potential problem); 2. When the density of charge is periodic and A has the form of the density function, then the potential in (12) is also periodic; and 3. Eqs. (12) may be applied generally in all cases: atoms, molecules and solids.

It should be noticed here, as was the case in the Slater work, that the functions ψ_i—although they differ from the exact solutions of the correlation problem—may give good results for energies in view of the fact that the calculation of the mean value of the energy over such a function gives values which have errors only of the second order in small quantities.

---

[10] There are some printing errors in Macke's paper which are removed by derivation of the formulas (10), as well as (1) and (8).

[11] See reference 2.

PHYSICAL REVIEW VOLUME 121, NUMBER 1 JANUARY 1, 1961

Temperature Dependence of the Nuclear Quadrupole Spectrum of Nb^{93} in Ferroelectric $KNbO_3$†

Robert R. Hewitt
Department of Physics, University of California, Riverside, California

(Received June 27, 1960; revised manuscript received September 1, 1960)

The nuclear electric quadrupole interaction of Nb^{93} in ferroelectric $KNbO_3$ has been measured as a function of temperature in the tetragonal, orthorhombic and rhombohedral phases. The values of $(1/\nu)(d\nu/dT)$ for these three phases are approximately -10^{-3}, -10^{-3}, and -10^{-4} per degree centigrade, respectively. In the tetragonal phase at 220°C, e^2qQ/h has been measured as 24 Mc/sec and the asymmetry parameter η is zero. An ionic calculation of field gradients in the tetragonal phase has been made including point charge and induced dipole contributions. The results of this calculation give the Sternheimer antishielding factor $(1-\gamma_\infty)$ as 15 in good agreement with its estimated value of $+16$. The temperature dependence of the electric field gradient at the Nb^{93} site as calculated from this ionic model is in agreement with the measured temperature dependence in the tetragonal phase.

I. INTRODUCTION

THE most successful model of ferroelectric behavior has been constructed for the perovskite ferroelectrics with the assumption of an electrostatic driving interaction. However, the validity of this model is critically dependent on the existence of an ionic environment for all of the crystal's constituent ions. Since an alternate mechanism for the perovskite ferroelectric behavior has been proposed by Megaw[1] where a covalent bond between the face-centered oxygen ions and the body-centered ions of this structure is to provide the ferroelectric driving action, it has become important to investigate the environment of the body-centered ion in these perovskite ferroelectrics.

$KNbO_3$ is a perovskite ferroelectric with four known crystal phases. Above 430°C it has a cubic structure. The oxygen ions in the face-centered position, form an octahedron about the body-centered niobium ions. The potassium ions are in the corners of the unit cell. As the crystal is cooled, its cubic, perovskite structure changes successively to tetragonal, orthorhombic and rhombohedral phases. The phase transitions occur at about 430°C, 220°C, and −50°C respectively. The structure changes occur by elongations along an edge

---

† Supported in part by the Office of Naval Research.

[1] H. D. Megaw, Acta Cryst. 7, 187 (1954).

of the unit cell, a face diagonal and then a body diagonal in that order with decreasing temperature.[2]

X-ray and neutron diffraction studies indicate the polarization in this type of structure occurs with the displacement of the face-centered ions in one direction and the body-centered ion in the opposite direction.[3–5] The lattice parameters as a function of temperature are known from 25°C to 510°C.[6] The dielectric constant as a function of temperature has been reported for all four phases.[7] The spontaneous electric polarization has been reported for the orthorhombic and tetragonal phases.[8]

Investigation of the central ion, Nb^{93}, by nuclear resonance has been undertaken in an attempt to obtain information about the nature of the forces acting on it in the ferroelectric phases. Earlier experiments with nuclear magnetic resonance and nuclear quadrupole resonance[9] showed large nuclear quadrupole interactions with crystalline electric field gradients. The pure quadrupole spectrum in the rhombohedral phase at −196°C and in the orthorhombic phase at about 40°C were measured in these earlier experiments.

The interaction of the electric quadrupole moment, Q, of the nucleus with the electric field gradient at the nucleus is given by,[10]

$$H=\frac{e^2qQ}{4I(2I-1)}(3\mathbf{I}_z^2-\mathbf{I}^2)+\eta(\mathbf{I}_x^2-\mathbf{I}_y^2), \tag{1}$$

where $eq=\partial E_z/\partial z$, the largest of the three field gradient axes, and η is the field gradient asymmetry parameter,

$$\left(\frac{\partial E_x}{\partial x}-\frac{\partial E_y}{\partial y}\right)\Big/\frac{\partial E_z}{\partial z}.$$

Since Nb^{93} has a spin of 9/2, there are five energy states. The transitions between states are induced by a weak rf magnetic field interacting with the magnetic moment of the nucleus and the usual selection rule of $|\Delta m|=1$ applies when $\eta=0$, but when the asymmetry is not zero, the selection rules are no longer restricted to $|\Delta m|=1$. In KNbO_3 the transition probabilities were too weak for $|\Delta m|>1$ to allow observation of these additional frequencies so in each case there are four resonances. The secular equation for $I=9/2$ was solved numerically by Cohen[11] for η in intervals of 0.1 from 0 to 1, and his solutions have been used to find the coupling constant e^2qQ/h and η from the four resonance frequencies in the orthorhombic phases. Since the nuclear quadrupole moment Q of Nb^{93} has been measured from optical hyperfine spectra,[12,13] the coupling constant provides a measure of $eq=\partial E_z/\partial z$ at the nuclear site to the precision of the measurement of Q.

As was first pointed out by Sternheimer,[14] the value of the field gradient outside of the ion is usually different than the field gradient at the nuclear site. The difference is effected by the interaction of the ion core electrons with the external charge distributions that produce the field gradient at the site of the nucleus. This effective magnification of the field gradient has a constant value and is included in the calculation of the gradients as the Sternheimer factor $(1-\gamma_\infty)$. It is apparent that this correction is not applicable to the measurement of Q from optical hyperfine spectra since in that case it is the energy differences between the electronic levels in a free ion that are measured.

Within a crystal phase, the temperature dependence of the resonance frequencies is produced by two interdependent mechanisms:

1. As first proposed by Bayer,[15] the thermal motions produce temperature dependent averaging of the static field gradients.
2. The thermal expansion of the lattice parameters produces a temperature dependence of the static electric field gradient.

Both processes contribute to the changes in resonant frequencies as a function of temperature. These two effects may be separable when both the temperature and the pressure dependence of the apparent field gradients are known.[16]

II. APPARATUS

A Pound spectrometer was used as the detector of nuclear quadrupole resonance (NQR).[17] The NQR was modulated with an antisymmetric square wave magnetic field[18] of about 200 oersteds.

The high temperatures were produced in a quartz Dewar with No. 22 Nichrome wire wound noninductively around the rf shield can. The rf coil forms, made of Lavite, were $1\frac{1}{4}$ inches long and $\frac{1}{2}$ inch in diameter and were wound with No. 30 bare copper wire. The wire was spaced with Fiberglas yarn and led to the top of the quartz Dewar through a double-hole ceramic rod. The copper wire was sealed from the air with Sauereisen cement. A standard high-temperature thermocouple of

---

[2] E. A. Wood, Acta Cryst. **4**, 353 (1951).

[3] W. Kanzig, Helv. Phys. Acta **24**, 175 (1951).

[4] H. T. Evans, Massachusetts Institute of Technology Laboratory for Insulation Research Technical Report No. 58, 1953 (unpublished).

[5] G. Shirane, R. Pepinsky, and B. C. Frazer, Phys. Rev. **97**, 1179 (1955).

[6] G. Shirane, R. Newnham, and R. Pepinsky, Phys. Rev. **96**, 581 (1954).

[7] G. Shirane, H. Danner, A. Pavlovic, and R. Pepinsky, Phys. Rev. **93**, 672 (1954).

[8] S. Triebwasser, Phys. Rev. **101**, 993 (1956).

[9] R. M. Cotts and W. D. Knight, Phys. Rev. **96**, 1285 (1954).

[10] T. P. Das and E. L. Hahn, in *Solid-State Physics* (Academic Press, Inc., New York, 1958), Suppl. 1.

[11] M. H. Cohen, Phys. Rev. **96**, 1278 (1954).

[12] D. R. Speck, Phys. Rev. **98**, 282 (1955).

[13] K. Murakawa, Phys. Rev. **98**, 1285 (1955).

[14] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

[15] H. Bayer, Z. Physik **130**, 227 (1951).

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

[17] R. V. Pound and W. D. Knight, Rev. Sci. Instr. **21**, 219 (1950).

[18] F. Reif and E. M. Purcell, Phys. Rev. **91**, 631 (1953).

platinum and an alloy of platinum plus 10% rhodium was placed just above the sample in the shield can for the measurement of the temperature. This thermocouple was calibrated for the temperature at the crystal site with a second thermocouple in the center of a ceramic block which had the approximate size and shape of the $KNbO_3$ crystal.

The low-temperature measurements were made in a double Pyrex Dewar. For measurements from 77°K to room temperature, liquid nitrogen was placed in the outer Dewar and allowed to evaporate; the sample warmed from 77°K to room temperature in about 48 hours. This rate of temperature change was sufficiently slow to allow measurements of resonant frequencies while the sample temperature changed less than 0.5°K. A similar method was used for obtaining measurements between 4.2°K and 77°K. Liquid helium was transferred to the inner Dewar and the sample was then warmed to 77°K. A copper-constantan thermocouple was used from 77°K to room temperature and gold-gold cobalt thermocouple was used from 4.2°K to 77°K. The precision of temperature measurement was different from these several methods. The measurements made at 4.2°K and 77°K were controlled to ±0.1°K. Since the sample warmed about 0.3°K during the 77°K to room temperature measurements and with an additional correction for temperature gradients, these temperatures were measured to ±1°K. Similar considerations gave the 4.2°K to 77°K range a precision of temperature measurement of ±2°K. Temperature stability problems in the high-temperature phase restricted the precision to ±1°K.

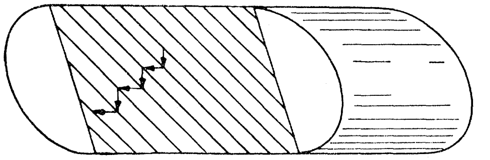

FIG. 1. A cut-out section of the single crystal II, showing the nature and direction of the laminar twinning in the orthorhombic phase. If 180° twinning is predominant in the tetragonal phase, the laminations will be perpendicular to those shown.

Frequency measurements were made with a BC-221 frequency meter to within 1 kc/sec.

III. RESULTS

Two $KNbO_3$ samples were used in these measurements; these samples are designated crystal I and crystal II in reference 9. Crystal I had been fractured extensively by repeated transitions from the orthorhombic to the rhombohedral phase and was ground into crystallites of about 1-mm dimensions for the measurements in the rhombohedral phase. Crystal II was in a cylindrical shape $\frac{1}{2}$ inch in diameter and had a mass of 7.6 g; an idealized sketch of its laminar domains and the directions of polarization are shown in Fig. 1. This single crystal was used for the measurements in the orthorhombic and tetragonal phases.

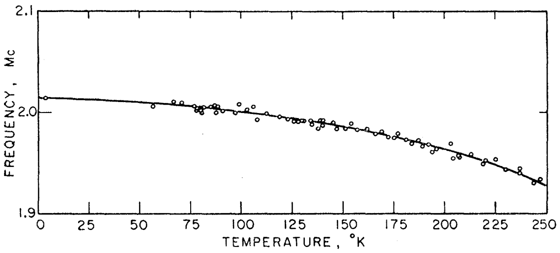

FIG. 2. Temperature dependence of the (7/2, 5/2) transition in the rhombohedral phase.

The temperature dependence of the (7/2, 5/2) transition in the rhombohedral phase from 4°K to about 250°K is shown in Fig. 2. Since the electric field gradient asymmetry η is zero for this phase, the quadrupole coupling e^2qQ/h can be calculated from a single frequency. Figure 3 is the resulting temperature dependence of e^2qQ/h, using the smoothed curve of Fig. 2 for the (7/2, 5/2) line.

In the orthorhombic phase, the (3/2, 1/2), (7/2, 5/2), and (5/2, 3/2) transitions are shown in Fig. 4 from about 35°C to the transition temperature, 220°C. The weaker (9/2, 7/2) line was traced for a 20°C interval but is not shown. The three lines are sufficient to calculate e^2qQ/h and η. The single point shown at 214°C for the (7/2, 5/2) line is not a reliable measurement due to a poor signal to noise ratio for this line near the transition temperature. The two dashed lines are representative of the uncertainty in this region. This uncertainty is carried into the calculated curves shown in Figs. 5 and 6. The parameters η and e^2qQ/h were calculated at 20°C intervals by fitting the smoothed, resonant frequencies in Fig. 4 to the calculations of Cohen[11] by the method described in reference 9. The resulting values of e^2qQ/h versus temperature and η versus temperature are shown in Figs. 5 and 6, respectively.

In the tetragonal phase, three of the four lines of the spectrum have been observed and are shown in Fig. 7. The (3/2, 1/2) line which should occur at about 1 Mc

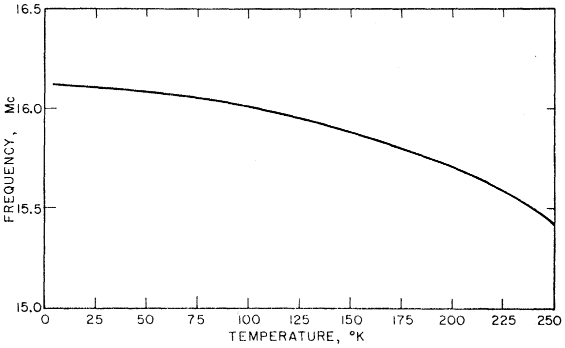

FIG. 3. Smoothed plot of e^2qQ/h vs temperature calculated from the data shown in Fig. 2.

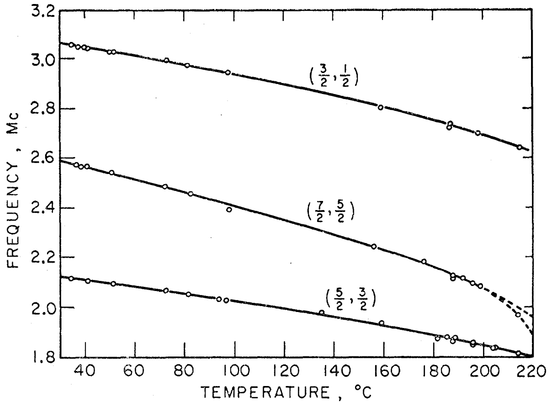

FIG. 4. Temperature dependence of three of the four transition frequencies in the orthorhombic phase.

was not investigated. The signal to noise ratio for the (5/2, 3/2) line was about 5 to 1 at the phase transition temperature of 220°C and became weaker as the temperature was raised until it was no longer visible above 420°C. The signal to noise ratio for the (9/2, 7/2) and (7/2, 5/2) lines was about 2:1 and they became very difficult to observe at higher temperatures. The low Q of the rf coils at these temperatures prevented the simultaneous observation of all three lines in a single coil. The (9/2, 7/2) and (7/2, 5/2) as well as the (7/2, 5/2) and (5/2, 3/2) lines were observed in pairs and the ratios of their frequencies were in agreement with an asymmetry of zero. Since the (5/2, 3/2) line was the strongest, it was used in the calculation of e^2qQ/h. e^2qQ/h is shown in Fig. 8 as a function of temperature.

Linewidths

No temperature dependence of the linewidths was observed in any of the phases studied. The precision of measurement of linewidth was approximately ±10%. The temperature range in the rhombohedral phase was from 4°K to 250°K. Throughout the phase, the half-amplitude linewidth of the (7/2, 5/2) transition remained at 30 kc/sec ±5 kc/sec, hence if there is any temperature dependence of this linewidth it is less than 0.05% per °C. No variation in linewidth greater than the precision of measurement was observed in the orthorhombic and tetragonal phases. The powdered sample had the same linewidths to within ±5 kc/sec as the single crystal.

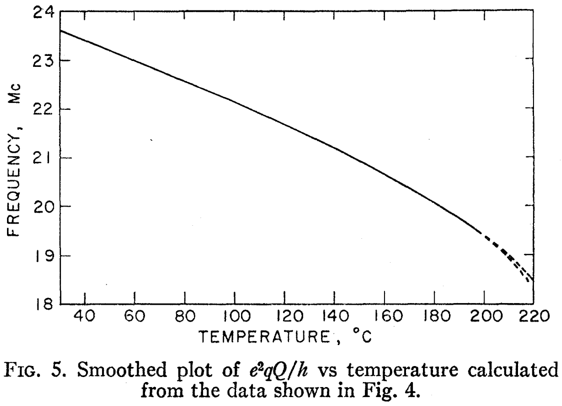

FIG. 5. Smoothed plot of e^2qQ/h vs temperature calculated from the data shown in Fig. 4.

A list of the linewidths at half maximum for the observed transitions in all three phases is given in Table I. The rhombohedral and orthorhombic phases were measured in previous work.[9]

IV. TEMPERATURE DEPENDENCE

The tetragonal phase is the simplest crystal phase and since the lattice dimensions and the spontaneous polarization have been measured for this phase throughout its temperature range, one would hope to obtain information about the source of the electric field gradient at the Nb site by comparing these parameters with the temperature dependence of the gradients.

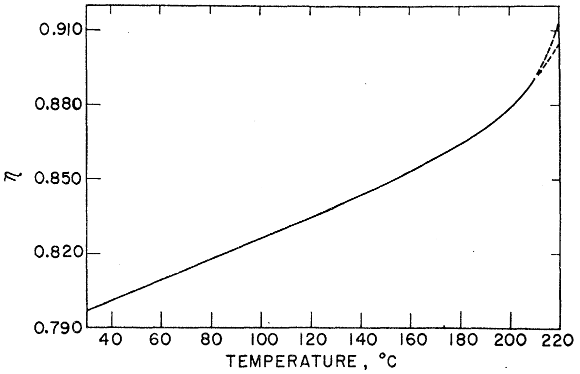

FIG. 6. Temperature dependence of the field gradient asymmetry parameter η in the orthorhombic phase as calculated from the data shown in Fig. 4.

A phenomenological equation for the temperature dependence of quadrupole interactions has been proposed by Kushida *et al.*[16]:

$$\frac{1}{\nu}\frac{\partial\nu}{\partial T_P}=\frac{V}{\nu}\left\{\frac{\partial\nu}{\partial q_0}\frac{dq_0}{dV}+\frac{\partial\nu}{\partial\eta_0}\frac{d\eta_0}{dV}+\sum_i\frac{\partial\nu}{\partial\zeta_i{}^0}\frac{\partial\zeta_i{}^0}{\partial V_T}\right\}\frac{1}{V}\frac{\partial V}{\partial T_P}+\frac{1}{\nu}\sum_i\frac{\partial\nu}{\partial\zeta_i{}^0}\frac{\partial\zeta_i{}^0}{\partial T_V},\quad(2)$$

where $\zeta_i{}^0$ are the amplitudes of the normal modes of vibration, ν is the observed resonance frequency, eq_0 is the static electric field gradient and η_0 is the static asymmetry parameter. The first term,

$$\frac{1}{\nu}\frac{\partial\nu}{\partial q_0}\frac{dq_0}{dV}\frac{\partial V}{\partial T_P},$$

is the temperature dependence of the electric field gradient produced by the change in the spatial distribution of the gradient sources as a function of temperature. The effect of this term will be calculated and discussed for an ionic model in Sec. V.

Since $\eta=0$ for the tetragonal phase and each ion type contributes to the field gradient with this axial symmetry, changes in thermal averaging will not change the symmetry, thus the second term,

$$\frac{1}{\nu}\frac{\partial\nu}{\partial\eta_0}\frac{d\eta_0}{dV}\frac{\partial V}{\partial T_P},$$

will be zero. There is no direct information on the third term,

$$\frac{1}{\nu}\sum\frac{\partial\nu}{\partial\zeta_i^0}\frac{\partial\zeta_i^0}{\partial V_T}\frac{\partial V}{\partial T_P};$$

however, the infrared absorption studies of Last[19] on several perovskites indicates that the changes in normal modes are rather small over a wide range of temperatures. The fourth term,

$$\frac{1}{\nu}\sum\frac{\partial\nu}{\partial\zeta_i^0}\frac{\partial\zeta_i^0}{\partial T}\bigg|_V,$$

is the Bayer motional averaging due to thermal vibrations.

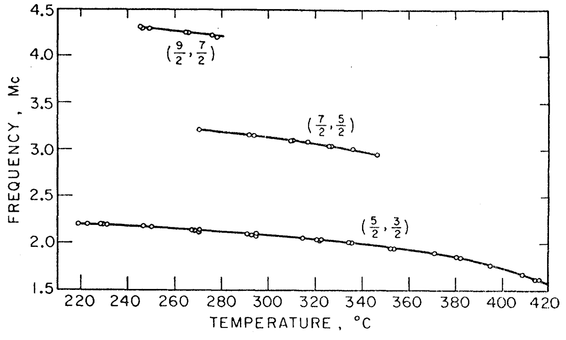

FIG. 7. Temperature dependence of three of the four transition frequencies in the tetragonal phase.

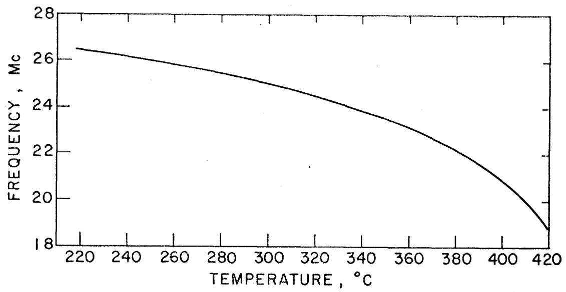

FIG. 8. Smoothed plot of e^2qQ/h vs temperature calculated from the data shown in Fig. 7 for the tetragonal phase.

The nature of this thermal averaging is seen from the approximation in the calculation of the quadrupole interaction given in Eq. (1) which assumes the electric field gradient q has a fixed value. The thermal motions of the ions at frequencies greater than the characteristic nuclear precessional frequencies in this environment will be effective as average values. These average values will depend on the temperature dependent lattice vibration spectrum. Since the ionic field gradient may be calculated for a point charge basis by a sum of the form[10]:

$$q=\sum_i\frac{3\cos^2\theta_i-1}{r_i^3},$$

the motional averaging may be calculated with the assumption of the Debye approximation in the summation of lattice modes. It is easily shown that for the high-temperature approximation, the vibration frequency $\nu<kT/h$ the temperature dependence of the ionic field gradient is given by[20]:

$$q=\sum_i\frac{(3\cos^2\theta_{0i}-1)}{a_i^3}\left\{1-\frac{15kT}{a_i^2\beta_i}\right\},\tag{3}$$

where the subscript 0 refers to the static value, k is Boltzman's constant, a_i is the distance to the ith ion and β_i is the force constant binding the ith ion.

TABLE I. Nb^{93} quadrupole linewidths in $KNbO_3$.

Transition	Rhombohedral width	Orthorhombic width	Tetragonal width
(9/2, 7/2)	25 kc	45 kc	40 kc
(7/2, 5/2)	30 kc	45 kc	50 kc
(5/2, 3/2)	30 kc	27 kc	30 kc
(3/2, 1/2)	...	30 kc	...

The force constants for various perovskites, including $KNbO_3$ in the orthorhombic phase, have been measured with infrared absorption by Last.[19] In these measurements the force constants were found to be of the order 10^5 dynes/cm^2. Substitution of the appropriate values in (3) with this value for the force constant gives a temperature dependence of 5×10^{-5} °C^{-1} for the contribution to $(1/\nu)(d\nu/dT_P)$. This magnitude of the temperature dependence represents a negligible contribution to the observed temperature dependence. This leaves the lattice expansion as the principal source of the temperature dependence and a consistent model of the field gradient sources should provide this dependence.

V. IONIC FIELD GRADIENTS

The tetragonal phase of the perovskite ferroelectrics has been investigated most extensively in the crystal $BaTiO_3$. In the following calculations, some of the work on $BaTiO_3$ will be used for the isomorphic crystal $KNbO_3$.

The ionic field gradient at the site of the nucleus can

---

[19] J. T. Last, Phys. Rev. **105**, 1740 (1957).

[20] M. Pomerantz, Ph.D. dissertation, University of California, Berkeley, 1957 (unpublished).

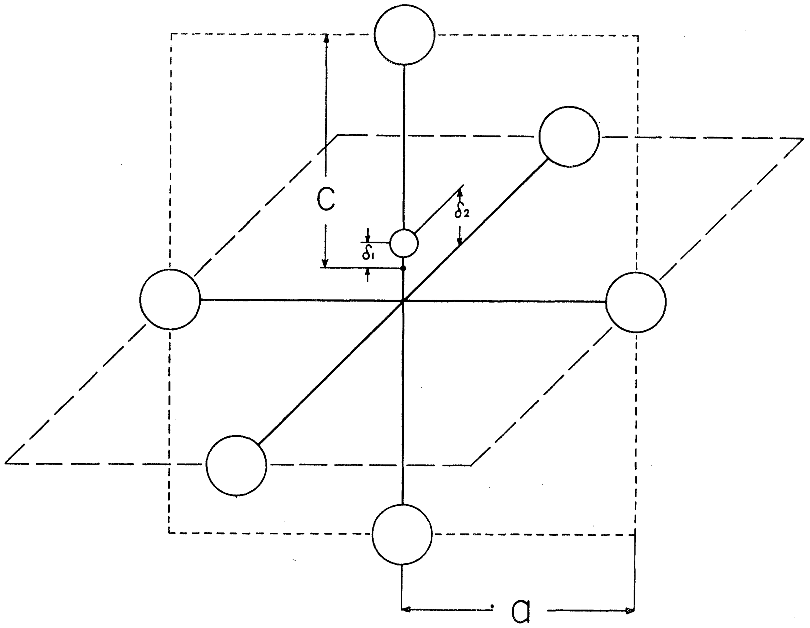

FIG. 9. The oxygen octahedron surrounding the Nb ion in the polarized tetragonal phase. The unit cell dimensions are $2a$ and $2c$. It is assumed that the two oxygens along the c axis have a different displacement than the other four.

be shown[21] to be given by

$$\frac{\partial E_z}{\partial z}=(1-\gamma_\infty)\sum_i{}'\frac{\partial^2}{\partial z^2}\left[\frac{q_i}{r_i}+\frac{\mathbf{u}_i}{r_i^2}+\frac{\mathbf{Q}_i}{r_i^3}+\cdots\right], \tag{4}$$

where $(1-\gamma_\infty)$ is the Sternheimer shielding factor,[14] q_i, u_i, and Q_i are the electric point charges, dipole moment and quadrupole moments, respectively, on the ith ion. The prime indicates that the sum excludes the ion at the site of the gradient calculation.

The point charge contribution to the Nb field gradient of the six surrounding oxygen ions, shown in Fig. 9 is given by

$$\frac{\partial E_z}{\partial z}=4e\left\{\frac{1}{(c-\delta_1)^3}+\frac{1}{(c+\delta_1)^3}-\frac{2}{(a^2+\delta_2^2)^{\frac{3}{2}}}\left[1-\frac{3\delta_2^2}{(a^2+\delta_2^2}\right]\right\}, \tag{5}$$

where $2e$ is the charge on each oxygen ion, $2c$ and $2a$ are the tetragonal axes, and δ_1 and δ_2 are the displacements of the two types of oxygens in respect to the niobium ion. Since δ_1 and δ_2 are an order of magnitude smaller than the tetragonal axes, this expression may be expanded for $\delta_1^2 \ll c^2$ and $\delta_2^2 \ll a^2$ as:

$$\frac{\partial E_z}{\partial z}\approx\frac{8e}{c^3}\left\{1-\left(\frac{c}{a}\right)^3\right\}+\frac{48e}{c^5}\delta_1^2+\frac{36e}{a^5}\delta_2^2. \tag{6}$$

Unfortunately, no measurements of the ionic displacements in $KNbO_3$ have been reported and the displacements must be estimated from the $BaTiO_3$ results. The same relative displacements per cell volume are assumed to exist in $KNbO_3$ as found in BaT_iO_3. Any error in the approximation will affect the total field gradient calculated but will have a negligible effect on the temperature dependence results since the temperature dependence of this contribution is about the same as the other terms. Assuming that the δ's in $KNbO_3$ are proportionally the same as those measured[22] by neutron diffraction in $BaTiO_3$, one finds from the $KNbO_3$ lattice dimensions[5] measured at 220°C:

$$a=2.00\text{ A},\quad \delta_1=0.144\text{ A},$$
$$c=2.03\text{ A},\quad \delta_2=0.108\text{ A},$$
$$c/a=1.0166.$$

These values give 2.32×10^{13}, 1.38×10^{13}, and 0.63×10^{13} esu, respectively, for the three terms in Eq. (6). Thus the effect of the polarization is not negligible in the point charge calculation.

A neutron diffraction study of $BaTiO_3$[23] near the Curie temperature showed that the ionic shifts δ_1, δ_2 as a function of temperature along the polar axis in the tetragonal phase were linearly proportional to the spontaneous polarization P_s. Merz has shown[24] experimentally that P_s^2 is proportional to $(c/a)-1$. On this basis, it will be assumed that δ^2 is proportional to $(c/a)-1$ in $KNbO_3$. Column I of Table II is the lattice contribution of the surrounding six oxygens to the Nb field gradient where δ_1 and δ_2 have been set equal to zero. The temperature points are chosen to coincide with the published lattice values. Column II is the

---

[21] Gerald Burns, Phys. Rev. **115**, 357 (1959).

[22] H. R. Danner, B. C. Frazer, and R. Pepinsky, Bull. Am. Phys. Soc. **2**, 23 (1957).

[23] H. R. Danner, B. C. Frazer, and R. Pepinsky, follows reference 2 in Bull. Am. Phys. Soc. **2**, 23 (1957).

[24] W. J. Merz, Phys. Rev. **76**, 1221 (1949); and **78**, 52 (1950).

TABLE II. Ionic electric field gradient contributions and a comparison of their temperature dependence fit to the measured interaction energy.

Temperature, °C	I Nearest neighbor calculation (10^{13} esu)	II Ionic displacement (10^{13} esu)	III Point charge IBM-704 sum. (10^{13} esu)	IV Electronic dipole (10^{13} esu)	V Sum of II, III and IV (10^{13} esu)	VI Measured e^2qQ (10^{-19} ergs)	VI $eQ(1-\gamma_\infty)$ (10^{-33} statcoulomb-cm^2)
220	2.32	2.01	2.34	5.18	9.53	1.751	1.84
230	2.32	2.01	2.34	5.18	9.53	1.744	1.83
270	2.29	1.99	2.32	5.11	9.42	1.698	1.80
320	2.15	1.87	2.20	4.78	8.85	1.622	1.83
375	2.00	1.73	1.92	4.42	8.07	1.490	1.85
410	1.70	1.48	1.50	3.76	6.74	1.252	1.86

contribution of the displacements according to their assumed temperature dependence.

The field gradient sum has been extended to all ions within a sphere with a radius of six lattice spacings, $12a$, in the tetragonal lattice where δ_1 and δ_2 have been set equal to zero. The calculations were made with the IBM-704 program developed by Bersohn.[25] To test the convergence of the sum, the value of the field gradients for ions within spheres of radius $6a$, $8a$, and $10a$ were also calculated. The lattice spacing is $2a$ in this calculation. At 220°C there was a decrease of 16% in q as the sum was extended from a radius of $6a$ to a radius of $12a$. The convergence is poorer with increasing temperature. At the 410°C point, there was a decrease of 22% in q for the same two radii. The decrease of q was monotonic for the four radii that were used. The values of q due to all ions within a volume of six lattice spacings is listed in column III of Table II.

The calculation of the induced electric dipole contributions to the field gradient again requires use of the measurements and calculations in $BaTiO_3$. The dipole contribution from (4) is given by:

$$\frac{\partial E_z}{\partial z}(\text{dipole})=\sum_i \frac{3\mu_i}{r_i^5}\left\{\frac{5z_i^2}{r_i^2}-3\right\}, \tag{7}$$

where μ_i is assumed to be in the direction of the z axis of the field gradient. The values of μ_i have been calculated for the tetragonal phase of $BaTiO_3$ by Triebwasser[26] using the spontaneous polarization and the internal field calculations of Kinase.[27] These results show that the only large electronic polarization is on the two oxygens in the unit cell which lie on the z axis passing through the titanium ion. A normalization of this result to the polarization per ion gives the electronic dipole moment. Assuming proportional results would be obtained in $KNbO_3$ and using the spontaneous polarization and lattice dimensions of $KNbO_3$, one calculates the electronic dipole moment on these two oxygens as 2.4×10^{-18} esu. The other ions in the unit cell and the next nearest oxygens give contributions that are an order of magnitude smaller.

Using (7) and taking the ionic polarization δ_1 shown in Fig. 9, the dipolar contribution of these two oxygens is:

$$\frac{\partial E_z}{\partial z}(\text{dipole})\approx\frac{48\mu\delta_1}{a^5}, \tag{8}$$

Substitution of the previously quoted values for the tetragonal phase of $KNbO_3$ at 210°C gives the dipolar contribution to q as 5.18×10^{13} esu in the same direction as the ionic contributions. Kinase has shown[27] that μ is proportional to δ; hence the dipolar contribution is proportional to δ_1^2/a^5 as seen from (8). In the point charge calculation above it was pointed out that for $BaTiO_3$, δ_1^2 is proportional to $(c/a)-1$; using this proportionality along with the above, q(dipolar) is proportional to $[(c/a)-1]/a^5$. This lattice dependence is then used to calculate the temperature dependence of the electronic dipolar contribution. These results are listed in column IV of Table II.

The resultant field gradient has been calculated by taking the sum of columns II, III, and IV and it is listed in column V. The calculations of these field gradients are based on the lattice dimensions that were reported by Shirane *et al.*[6] The values of the measured e^2qQ at the six temperatures that the lattice dimensions have been reported are listed in Column VI of Table II.

The test of the temperature dependence of this model is made by dividing the measured e^2qQ by the calculated eq. This ratio should be $e(1-\gamma_\infty)Q$ and it should be independent of temperature. The ratios are listed in column VII.

A comparison of the magnitude of the field gradient may be made only qualitatively. The quadrupole moment of Nb has been measured from optical hyperfine spectra as $(-0.4\pm0.3)\times10^{-24}$ cm^2 and $(-0.25\pm0.1)\times10^{-24}$ cm^2.[12,13] $(1-\gamma_\infty)$ has been estimated[28] as $+16$ for 5^+Nb. Using -0.25×10^{-24} cm^2 for Q and the calculated value of q at 220°C, one obtains a value of 15 for $(1-\gamma_\infty)$.

Similar calculations of the ionic field gradients in the orthorhombic phase have been made. These calculations

---

[25] R. Bersohn, J. Chem. Phys. **29**, 326 (1958).

[26] S. Treibwasser, J. Chem. Phys. Solids **3**, 53 (1957).

[27] W. Kinase, Progr. Theoret. Phys. (Kyoto) **13**, 529 (1955).

[28] Gerald Burns, J. Chem. Phys. **31**, 1253 (1959).

included nearest neighbor dipole contributions and used the IBM-704 program for point charge contributions. The results were found to be extremely sensitive to variations in ionic displacements. Because of the lack of information on the nature of electronic polarizations and ionic displacements, no consistent results were obtained. In the models that assumed displacements proportional to the orthohombic $BaTiO_3$, the electronic dipole contributions were the same order of magnitude as the point charge contributions to the field gradient. The field gradient asymmetry parameter η is a sensitive function of these displacements with any value from 0 to 1 being possible, depending on the displacements used.

No calculations have been made on the rhombohedral phase.

VI. DISCUSSION

The calculations of the electric field gradient in the tetragonal phase are dependent upon the assumption of identical ionic polarizations in the tetragonal phases of $KNbO_3$ and $BaTiO_3$. If this assumption is in error, it would change the magnitude of the electric field gradient, but it would not appreciably affect the fit of the temperature dependence. With this qualification, the temperature dependence and the magnitude of e^2qQ in the tetragonal phase are in agreement with the assumption of an ionic environment for the niobium ion. The extension of this calculation to the orthorhombic phase would give a further internal check on the validity of the model since the size of $(1-\gamma_\infty)Q$, the two least accurately known parameters in this interaction, should be the same in both phases. A more complete investigation of the type made here including neutron diffraction, x-ray diffraction, and NQR on the same crystal of $KNbO_3$ would eliminate the probable objections to the approximation in the calculation. Such an extensive effort is not planned since a fit to the ionic model is provided to the precision of the present measurements of Q.

The successful calculation of the field gradients in the orthorhombic phase requires neutron diffraction measurements in $KNbO_3$ to determine the ionic displacements. These results could then be used in a calculation of the type made by Kinase and Triebwasser for the tetragonal phase of $BaTiO_3$.

A further test of the nature of the niobium field gradient is to be made by measuring its volume dependence at constant temperature. These pressure measurements are now in progress and will be reported at a later date.

An objection to the use of this result as evidence of an ionic environment in the perovskite structures is that only one of the ferroelectric perovskites has been investigated. A similar investigation of $BaTiO_3$ has been proposed but at present it appears that the lower abundance of Ti^{47} and Ti^{49} and their smaller magnetic moments would provide a difficult signal to noise ratio. It is possible that this method can be extended to other ferroelectrics and antiferroelectrics if there were sufficient measurements of the crystal structures and their temperature dependence.

ACKNOWLEDGMENTS

I extend my thanks to R. L. Fulton for making the IBM-704 calculations used in this paper.

I am indebted to G. Burns, T. P. Das, M. Pomerantz, and E. G. Wikner, for their suggestions and assistance in the calculation of the field gradients. In particular, I wish to extend my gratitude to Professor W. D. Knight whose suggestion of this problem and continued assistance has made this work possible.