has calculated the electron mobility for polar lattice scattering. The calculated room-temperature mobility is 7000 cm^2/volt sec which is in reasonable agreement with experimental values for the purest samples.[11]

The λ^3 dependence of the absorption coefficient at longer wavelengths is similar to that which has been reported for n-type InAs.[17] The dependence of the absorption on carrier concentration indicates the probable presence of some impurity-scattering absorption.[18] The λ^3 dependence of the absorption is close to that which is theoretically predicted by Fan[18] and by Meyer[19] for impurity-scattering absorption. However, at the present time, theoretical calculations have not been made for the spectral shape of the lattice-scattering absorption in partially polar semiconductors.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Mr. G. Sorin who aided in some of the infrared measurements and Mr. J. A. Ditzenberger who assisted in the preparation of some of the crystals. We are also indebted to Dr. D. A. Kleinman and Dr. H. Ehrenreich for several interesting discussions on this work.

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[17] J. R. Dixon and D. P. Enright, Bull Am. Phys. Soc. Ser. II, 3, 255 (1958).

[18] Fan, Spitzer, and Collins, Phys. Rev. **101**, 566 (1956).

[19] H. J. G. Meyer, Phys. Rev. **112**, 298 (1958).

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Study of Ferroelectric Transitions of Solid-Solution Single Crystals of $KNbO_3$-$KTaO_3$

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Methods of preparation and results of measurements of the dielectric constant of solid-solution single crystals of $KNbO_3$ and $KTaO_3$ are presented. Data are given for the composition range 0–80 mole percent $KTaO_3$ in the temperature interval -180°C to 450°C. It is found that all of the crystals studied show Curie-law behavior of the dielectric constant in the paraelectric state. The data indicate that the paraelectric to ferroelectric transition, which is first order for pure $KNbO_3$, becomes second order at a concentration of approximately 55 mole percent $KTaO_3$. Analysis of the results in terms of Slater's model of ferroelectricity in a perovskite lattice leads to the conclusion that the dependence of the Lorentz correction on volume plays a major role in determining the ferroelectric behavior. Ionic polarizabilities and their dependence on volume are also discussed.

I. INTRODUCTION

At the present time, more than ten years after the discovery of ferroelectricity in $BaTiO_3$, a large body of data has been accumulated not only on this perovskite-type crystal, but on several others, both ferroelectric and antiferroelectric in behavior. The reader is referred to Kaenzig's[1] excellent review of the subject which lists many references. The experimental data has been described and explained rather successfully by a phenomenological theory developed in some detail be Devonshire.[2] Slater[3] extended this theory and showed how the observed dependence of the free energy on temperature and electric polarization could be derived accurately from a consideration of the ionic structure of the lattice and the calculated internal Lorentz field. Further examination of Slater's model by this author[4] indicated that the important details of the experimental facts could be predicted at least qualitatively by improving the model somewhat. The present state of the theory is such as to provide order of magnitude agreement with the observed data, but in view of present uncertainties of the details of the bonding structure and short range interactions of the atoms in the lattice it appears that quantitative explanations cannot be made.

The present study was motivated by a desire to study the effect of the variation of a structural parameter in a perovskite ferroelectric. $KNbO_3$ is a ferroelectric exhibiting a transition from a cubic paraelectric to tetragonal ferroelectric state at ~700°K.[5] $KTaO_3$ has a transition, structural details of which are not known at present, from paraelectric to ferroelectric state at 13°K.[6] At 450°C, a temperature at which both materials are cubic, the lattice parameter of $KNbO_3$ is 4.0226 A while for $KTaO_3$ it is 4.0026 A.[7] It was felt that solid solutions of these two components would generate a lattice in which the structural perturbations would be

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[1] W. Kaenzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4.

[2] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949).

[3] J. C. Slater, Phys. Rev. **78**, 748 (1950).

[4] S. Triebwasser, J. Phys. Chem. Solids **3**, 53 (1957).

[5] B. T. Matthias and J. P. Remeika, Phys. Rev. **82**, 727 (1951).

[6] Hulm, Matthias, and Long, Phys. Rev. **79**, 885 (1950).

[7] M. Berry and F. Holtzberg (private communication).

small enough to warrant using the pure material as the model.

II. PREPARATION OF MATERIALS

From an examination of ionic radii of Ta and Nb and the cell constants of $KNbO_3$ and $KTaO_3$, it was expected that the latter two materials would form a continuous series of solid solutions over the entire composition range. To verify this, the phase diagram of $KNbO_3$-$KTaO_3$ was investigated.[8]

Solid-solution ceramics were prepared, but it soon became apparent that really good dielectric data required better ceramics than we were able to produce. From the information given in the phase diagram shown in Fig. 1,[9] it is possible to grow a single crystal of any desired composition. For example, a crystal having the composition B can be grown from a melt having the composition A by cooling to T_A at which point material of composition B crystallizes. If the temperature were lowered to $T_A - \Delta T$ further crystallization would occur with accompanying enrichment of the solid phase with the lower melting component, $KNbO_3$. To minimize this effect ΔT is kept small by growing a small crystal from a large charge of molten material.

In detail, the crystals were grown from a melt in a Pt crucible. The solution was seeded using a small $KTaO_3$ crystal suspended on a Pt wire. When approximately 5% of the mass of the solution had deposited, the cooling was stopped and the crystal kept submerged in the liquid for about twenty-four hours. The crystal was then raised above the melt and the furnace cooled to room temperature at a rate of about 10°C per hour. The actual growing process took about twenty-four hours, using cooling rates of fractions of a degree per hour. Thermal regulation to ~0.1°C for prolonged periods was maintained by a system described elsewhere.[10]

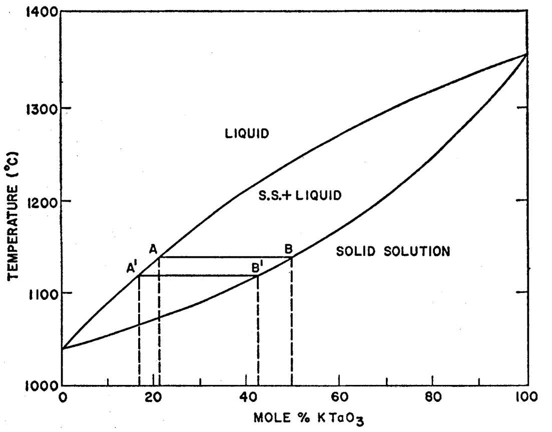

FIG. 1. Phase diagram $KNbO_3$-$KTaO_3$.

The purpose of the slow growth and subsequent soak was to permit time for the crystal to achieve homogeneity. Rapid growth from a system exhibiting the phase diagram shown in Fig. 1 leads to a crystal containing a concentration gradient of the constituents, unless diffusion takes place very rapidly.

The concentration and homogeneity of crystals obtained in the manner described was verified by an intercomparison of three pieces of information; (1) predicted concentration taken from the growth temperature and the phase diagram, (2) the density of the crystal, (3) the position and sharpness of the ferroelectric transition observed by dielectric constant measurements. The relation between density and concentration and transition temperature and concentration are taken from published data on ceramics.[11] The values of concentration of $KTaO_3$ and $KNbO_3$ in a given crystal derived from these three independent observations usually agreed with each other to within 2 or 3%, so that uncertainty in concentration may be taken as 3% by molecular weight.

The most sensitive check of the homogeneity of the samples is found in the plot of the dielectric constant as a function of temperature. The ceramics generally showed quite rounded peaks, with the maximum dielectric constant generally falling with increased concentration of $KTaO_3$. Single crystals, on the other hand, exhibit sharp transitions and increasing peak dielectric constant with increasing concentration of $KTaO_3$.

Writing the chemical formula of the solid solution as $KTa_fNb_{1-f}O_3$, measurements reported here are given for the range from $f=0$ to $f=0.8$. Samples with $f=1.0$ (pure $KTaO_3$) have been prepared but measurements have been made only as low as -180°C which is well above the range of interest for $KTaO_3$. Some data on pure $KTaO_3$ near liquid helium temperature are available in the literature.[12] Barrett[13] has indicated that quantum effects are important in this region so that the general conclusions drawn from this data would not be valid since they are based on an essentially classical model.

III. THE DIELECTRIC CONSTANT

Single crystals were grown in the form of plates of the order of $\frac{1}{4}$ in.$\times\frac{1}{4}$ in.$\times\frac{1}{8}$ in. with (100) faces. Some of the measurements were made by completely electroding opposite faces. This provides the severest test of crystalline homogeneity since a crystal with a concentration gradient would have an ill-defined transition temperature. Other measurements were made by

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[8] Reisman, Triebwasser, and Holtzberg, J. Am. Chem. Soc. **77**, 4228 (1955).

[9] Reference 8, Fig. 2.

[10] G. R. Gunther-Mohr and S. Triebwasser, IBM J. Research Develop. **1**, 84 (1957).

[11] A. Reisman and E. Banks, J. Am. Chem. Soc. **80**, 1877 (1958).

[12] Hulm, Matthias, and Long, Phys. Rev. **79**, 885 (1950).

[13] J. H. Barrett, Phys. Rev. **86**, 118 (1952).

cutting 0.010-in. slices from a crystal and evaporating round gold electrodes on the faces. The latter samples are far less susceptible to damage due to strain associated with undergoing phase transitions.

To examine the ferroelectric transition in detail and to locate the tetragonal to orthorhombic and orthorhombic to rhombohedral transitions, a previously described[14] method of plotting ϵ *vs* temperature on an X-Y recorder was employed. To measure the reciprocal Curie constant and T_0 as described below, capacitance was generally measured with a bridge over a range of temperatures above the paraelectric to ferroelectric transition point.

In Fig. 2 are shown results of measurements of the dielectric constant of single crystals having the indicated concentration of $KTaO_3$. There are several qualitative observations that can be made from the data:

(1) The Curie point moves to lower temperatures with increased $KTaO_3$ concentration.

(2) The peak dielectric constant increases with increasing $KTaO_3$ concentration.

(3) The thermal hysteresis between heating and cooling curves generally decreases with increasing $KTaO_3$ concentration.

A quantitative analysis of the results is facilitated by describing the behavior in terms of the phenomenological treatment proposed by Devonshire.[2] The free energy of the stress free crystal may be written:

$$F(P,T)=AP^2+BP^4+CP^6+\cdots+F_0(T), \tag{1}$$

where P is the polarization, T the temperature, $F_0(T)$ includes the part of the free energy which is essentially polarization independent, and A, B, and C are coefficients which are in general functions of temperature.

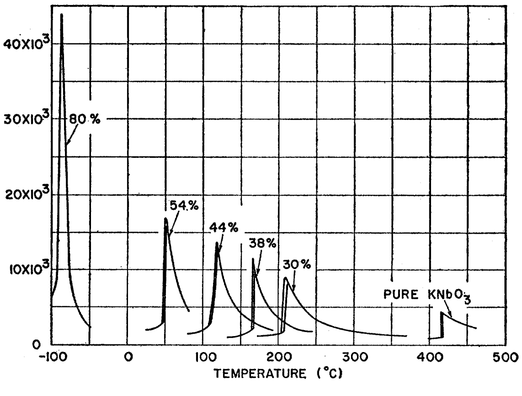

FIG. 2. Dielectric constant *vs* temperature for solid solution single crystals of $KTaO_3$ and $KNbO_3$. The indicated percentages are in moles of $KTaO_3$. Measuring field is ~5 v/cm and 10 kc/sec.

Thermodynamically it can be shown[15] that

$$\partial F/\partial P=E;\quad \partial^2F/\partial P^2=4\pi/(\epsilon-1), \tag{2}$$

where E is the electric field and ϵ the dielectric constant.[16] In the paraelectric state ($P=0$)

$$\epsilon-1=4\pi/2A. \tag{3}$$

Experimentally, it has been found for the ferroelectrics to which this analysis has been applied that the temperature dependence of A can be written explicitly:

$$A=A'(T-T_{cp}), \tag{4}$$

where A' is temperature independent, and T_{cp} is the paraelectric Curie temperature. Practically, for the measurements reported here, $\epsilon>10^3$, so that the approximation $\epsilon-1=\epsilon$ will be used. Then we can write

$$\epsilon=\frac{2\pi}{A'}\frac{1}{(T-T_{cp})}=\frac{c}{T-T_{cp}}, \tag{5}$$

where c is the Curie constant. If ϵ^{-1} is plotted as a function of the temperature in the paraelectric state, the resulting straight line yields values of T_{cp} and A'.

The maximum of $\epsilon(\epsilon_{\max})$ occurs at the transition temperature (T_{cf}) and is given by

$$\epsilon_{\max}=2\pi/[A'(T_{cf}-T_{cp})]. \tag{6}$$

In the case that B is positive $T_{cf}=T_{cp}$,[15] $\epsilon_{\max}$ is infinite,[17] and the ferroelectric transition is second order[15,17]. In the case that B is negative, $T_{cf}>T_{cp}$ and is related to A', T_{cp}, B, and C by[18]

$$A'(T_{cf}-T_{cp})=B^2/4C. \tag{7}$$

In this case the transition is first order.

Figure 3 shows $1/\epsilon$ *vs* T for a number of samples of various compositions. From these data, A' and T_{cp} can be found. Figure 4 shows A' as a function of the $KTaO_3$ concentration. Figure 5 shows the temperature of transitions observed in these crystals and the values of T_{cp} taken from Fig. 3 plotted as a function of composition. Where thermal hysteresis is observed the transition temperature is taken as midway between the heating and cooling transition temperatures.

A number of conclusions can be drawn from the data related to the various coefficients in Eq. (1): the constant A' increases with increasing concentration of $KTaO_3$, while the temperature T_{cp} decreases and $(T_{cf}-T_{cp})$ decreases. Further, it is seen that the peak

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

[15] For a discussion of most of the thermodynamic relations used in this paper, see A. F. Devonshire, Advances in Physics, edited by N. F. Matt (Taylor and Francis, Ltd., London, 1954), Vol. 3, p. 85, Sec. 3.

[16] The equations are written in unrationalized Gaussian units where $D=\epsilon E=E+4\pi P$, and $\frac{1}{4}\pi$ may be written whenever ϵ_0 appears.

[17] For an example of this, see S. Triebwasser, IBM J. Research Develop. **2**, 212 (1958).

[18] See reference 14, appendix.

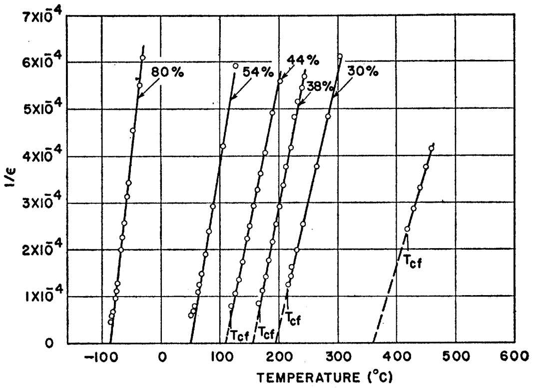

FIG. 3 $1/\epsilon$ *vs* temperature for solid solution single crystals of $KTaO_3$ and $KNbO_3$. The indicated percentages are in moles of $KTaO_3$. Measuring field is ~5 v/cm and 10 kc/sec. The indicated T_{cf} values are the observed transition temperatures to the ferroelectric state.

dielectric constant, which is related to both $(T_{cf}-T_{cp})$ and A', increases.

Phenomenologically it appears that replacing Nb ions with Ta ions, changes the nature of the ferroelectric transition from first to second order. This is a consequence of the fact that the sign of B changes from negative to positive. This would also explain the observed increase in $\epsilon_{\max}$ as seen from Eqs. (6) and (7). When B becomes positive, $(T_{cf}-T_{cp})$ is zero and the ferroelectric transition becomes second order. In this case the theoretical $\epsilon_{\max}$ is infinite, but the observed $\epsilon_{\max}$ depends on factors not intrinsic to the ideal material such as homogeneity of the sample, quality of electrodes, and amplitude of the measuring signal.

Figure 6 shows the variation of the dielectric constant with temperature of a sample of $KNb_{0.2}Ta_{0.8}O_3$ displaying all three transitions. The observed thermal hysteresis in order of decreasing temperature are 0, ~0, and 3°C. In pure $KNbO_3$ the observed thermal hysteresis for the same three transitions is 5°C, 15°C, and 25°C.[19]

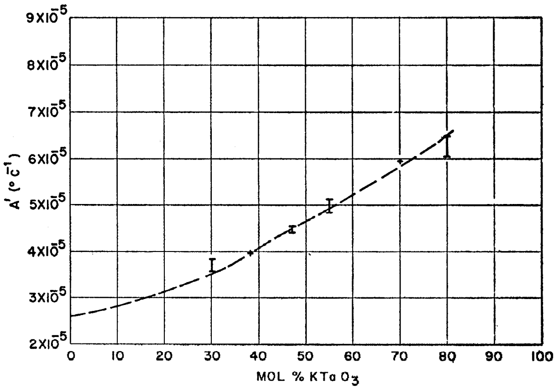

FIG. 4. A' *vs* composition. Where spread of values is shown a number of different crystals contributed to the value. The point for 0% $KTaO_3$ is taken from reference 14.

It can be shown[15] that for a second order ferroelectric transition, the absolute value of the ratio of the slopes of the reciprocal dielectric constant as a function of temperature just below the transition is twice that just above. Figure 7 shows such data for a crystal of the same composition ($KNb_{0.2}Ta_{0.8}O_3$). The dashed line to the left of the transition temperature is that predicted from the data above the transition temperature. The different character of the transition in material of this composition from that of pure $KNbO_3$ is also apparent from Fig. 2.

If we wish to classify the "strength" of a ferroelectric transition qualitatively, a negative B means that the cell has a strong tendency to become noncubic. A positive B coefficient leads to a "weaker" ferroelectric transition and much smaller strain on the crystal on going through its transition.

Data on spontaneous polarization is desirable in order to complete the analysis of the behavior of the B coefficient. Unfortunately, the results were not judged sufficiently reliable in the regions of interest (namely in the vicinities of transitions) due primarily to excessive conductivity of the crystals. The inset in Fig. 6 shows an example of one of the better hysteresis loops observed.

IV. THEORY OF THE SOLID-SOLUTION DIELECTRIC BEHAVIOR

Considerable quantitative information can be derived from the dielectric data. To derive the results given below a model similar to that proposed by Slater[3] will be assumed. If the chemical formula of the perovskite is written ABO_3, then the atom occupying the A position and the oxygen atoms are assumed to have only electronic polarizability (ionic polarizabilities are zero) designated by α_A and α_0, respectively. In addition, these quantities are assumed to be independent of volume, temperature and composition of the lattice. The polarizability in the B site, α_B, on the other hand, is a function of all of these. Since the unit cell volume, V, is a function of T and f, V appears as a dependent

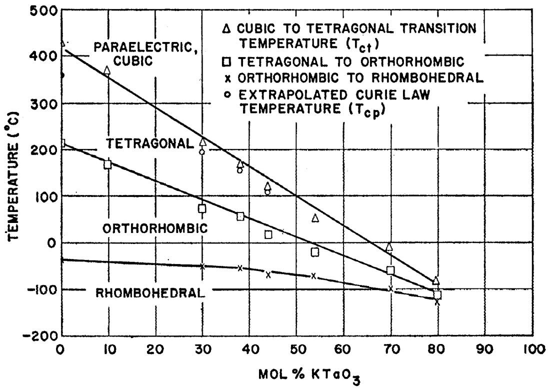

FIG. 5. Transition temperatures and T_{cp} as a function of composition in $KTaO_3$-$KNbO_3$ solid solution.

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

variable in the analysis that follows. It will be demonstrated that this parameter (volume) plays a major role in determining the behavior of the perovskite.

Using a method and model essentially the same as that used by Slater, Granicher and Jakits[20] examined the dielectric properties of a number of solid-solution perovskites. They used the values of ϵ at room temperature to calculate apparent polarizabilities of constituent ions in a number of pure and mixed perovskites. In attempting to predict the behavior of a particular solid solution on the basis of their calculations, they found that the simple model which uses the derived polarizability of an ion in one crystal to calculate ϵ in another breaks down. The conclusion they reached is that the ionic polarizability is a strong function of interionic distances. The results given below certainly bear out their conclusions.

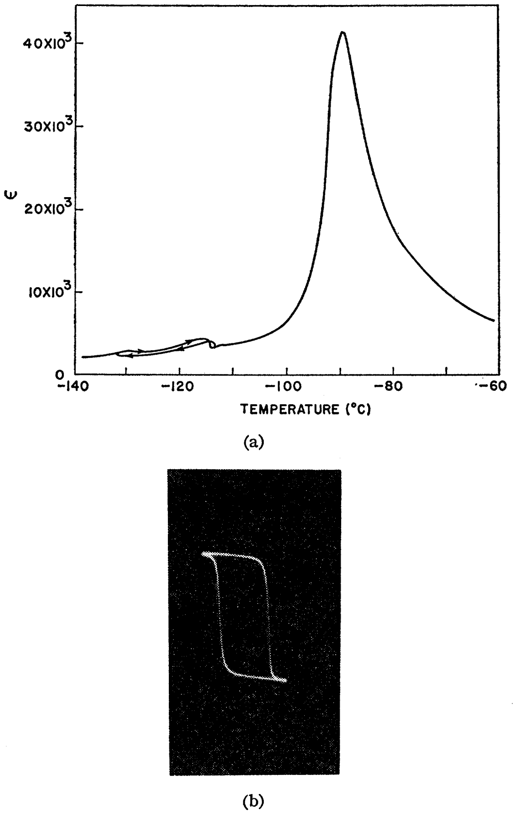

FIG. 6. (a) Dielectric constant *vs* temperature in $KTa_{0.8}Nb_{0.2}O_3$. Crystal is plate 0.17 cm×0.095 cm×0.016 cm thick, completely electroded on faces. (b) is oscilloscope trace of 60-cps sine wave hysteresis loop at −167°C; spontaneous polarization is 9.7 μcoul/cm² and coercive field is 0.6 kv/cm.

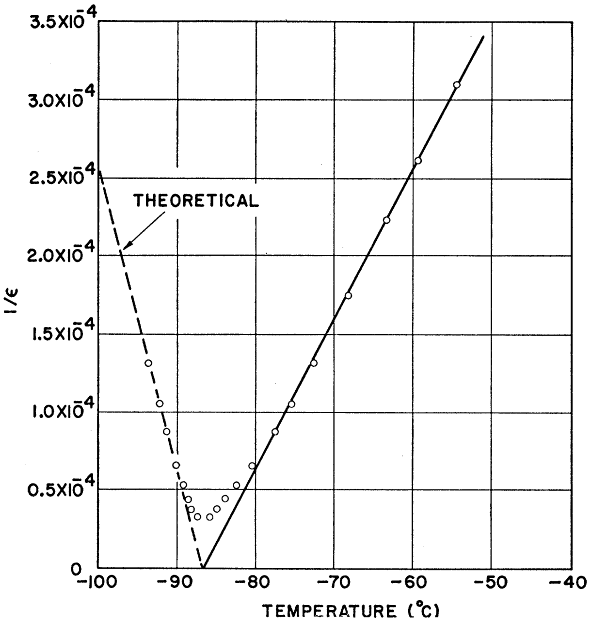

FIG. 7. $1/\epsilon$ *vs* temperature for sample of composition $KTa_{0.8}Nb_{0.2}O_3$. The dashed line to left of transition was drawn with a slope double that to the right and passing through the same point on the abscissa.

To analyze the experimental results, Slater's notation will be used. The input data will be observed dielectric data and the volumetric results taken from x-ray data. Calculations are restricted to the cubic (paraelectric)[21] phase. Slater[3] shows [Eq. (24)] that for a cubic perovskite lattice the dielectric constant is given by

$$\epsilon-1=\frac{c_2}{c_4}+\frac{(c_1/c_3)-(c_2/c_4)}{1+(c_4/c_3)(\alpha_B/\epsilon_0 V)},\qquad(8)$$

where c_1, c_2, c_3, and c_4 are functions of the electronic polarizabilities of the ions and the volume of the unit cell and α_B is the ionic polarizability of the atom in the B site and V the volume of the unit cell. If we let α_B be the total polarizability in the B site, then the c's are modified as follows (taking account of a term omitted in Slater's expression for c_1):

$$c_1=X_A+3X_0+pX_AX_0-8p^2X_AX_0^2+3pX_0^2,\qquad(9a)$$

$$c_2=1+pX_0-\tfrac{3}{2}(p+q)^2X_AX_0-\tfrac{1}{2}(3q-p)X_0^2,\qquad(9b)$$

$$\begin{aligned}c_3=1-\tfrac{1}{3}X_A+(p-1)X_0-p[\tfrac{1}{3}+\tfrac{3}{2}p]X_AX_0&\\-p(1+\tfrac{1}{2}p)X_0^2+(8/3)p^2X_AX_0^2,&\qquad(9c)\end{aligned}$$

$$\begin{aligned}c_4=-\tfrac{1}{3}-[\tfrac{1}{3}p+\tfrac{3}{2}q^2]X_0+\tfrac{1}{6}(3q-p)^2X_0^2&\\+\tfrac{1}{2}(p+q)^2X_AX_0,&\qquad(9d)\end{aligned}$$

where $X=\alpha/\epsilon_0 V$, $p=0.690$, and $q=2.394$. A more detailed solution has been worked out[4] in which ionic polarizability of all atoms is taken into account, but for the purpose of this discussion the additional complications serve only to becloud the results.

Using Slater's value of α_0 and a value of α_A (the A

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[20] H. Granicher and O. Jakits, Nuovo cimento **11**, 480 (1954).

[21] Applicability of the free-energy function observed in the paraelectric phase to describe and predict the ferroelectric behavior of $BaTiO_3$ and $KNbO_3$ has been demonstrated by various authors. See references 2, 14, and M. E. Drougard and E. J. Huibregtse, IBM J. Research Develop. **1**, 318 (1957).

TABLE I. Data pertinent to the calculation of β, $\partial\beta/\partial T$, and $\partial\beta/\partial f$.

% KTaO$_3$	f	A' (°C^{-1})	T_{cp} (°C)	V_{cp} (A^3)	$(\partial V/\partial T)_f$ (A^3°C^{-1})	$(\partial V/\partial f)_T$ (A^3)	$[(c_4/c_3)(1/V)]$ (A^{-3})	$\frac{\partial}{\partial V}[(c_4/c_3)(1/V)]$ (A^{-3})^2	$(c_1/c_3)-(c_2/c_4)$
0	0	2.6×10^{-5}	360	64.905	-1.98×10^{-3}	-0.77	-6.80×10^{-2}	$+0.24\times10^{-2}$	1.62
20	0.2	3.1×10^{-5}	245	64.573	-1.56×10^{-3}	-0.64	-6.88×10^{-2}	$+0.24\times10^{-2}$	1.63
40	0.4	4.1×10^{-5}	135	64.291	-1.31×10^{-3}	-0.64	-6.95×10^{-2}	$+0.24\times10^{-2}$	1.65
60	0.6	5.2×10^{-5}	20	64.013	-1.15×10^{-3}	-0.77	-7.02×10^{-2}	$+0.24\times10^{-2}$	1.66
80	0.8	6.5×10^{-5}	-90	63.715	-1.11×10^{-3}	-0.96	-7.09×10^{-2}	$+0.24\times10^{-2}$	1.68

atom here is K$^+$) taken from Tessman *et al.*,[22] we find

$$\alpha_0/\epsilon_0 = 30.0\ \mathrm{A}^3,$$
$$\alpha_A/\epsilon_0 = 16.8\ \mathrm{A}^3.$$

The values of c_1, c_2, c_3, and c_4 were calculated over the range $V = 63.0$ A^3 to 65 A^3.

The observed dielectric data must now be compared with Eq. (8). In the vicinity of the transition, ϵ is large as is the second term on the right of Eq. (8). If we define $\beta = \alpha_B/\epsilon_0$ and $(c_4/c_3)(1/V) = \gamma$, then Eq. (8) can be rewritten to good approximation as

$$\epsilon = \frac{(c_1/c_3)-(c_2/c_4)}{1+\gamma\beta} \tag{8$'$}$$

where β is now used in the sense of an average polarizability associated with the mixture of Nb and Ta atoms occupying the B site. There is an assumption made here that the local field at this site is independent of the occupant of the site, and conversely, its contribution to the polarization is simply summed over the two possible random occupants of that site.

The observed dielectric data as described by Eq. (5) must now be reconciled with Eq. (8′). The conditions required are:

$$\gamma\beta = -1 \quad \text{at} \quad T = T_{cp}, \tag{10}$$

and

$$\frac{\partial}{\partial T}\left(\frac{1}{\epsilon}\right) = \frac{2A'}{4\pi} = \frac{\partial}{\partial T}\left[\frac{1+\gamma\beta}{(c_1/c_3)-(c_2/c_4)}\right] \tag{11}$$

for a given f. We can then write

$$d(\gamma\beta) = \frac{\partial}{\partial T}(\gamma\beta)dT + \frac{\partial}{\partial f}(\gamma\beta)df, \tag{12}$$

or, if we constrain the variations so that Eq. (10) is always satisfied:

$$0 = \frac{\partial}{\partial T}(\gamma\beta)\frac{dT_{cp}}{df} + \frac{\partial}{\partial f}(\gamma\beta), \tag{13}$$

where dT_{cp}/df is the observed variation of T_{cp} with f.

Explicitly, Eqs. (11) and (13) may be written:

$$\frac{A'}{2\pi} = \left[\left(\frac{c_1}{c_3} - \frac{c_2}{c_4}\right)\right]^{-1}\left[\beta\left(\frac{\partial\gamma}{\partial V}\right)\left(\frac{\partial V}{\partial T}\right) + \gamma\left(\frac{\partial\beta}{\partial T}\right)\right], \tag{14}$$

and

$$0 = \left[\beta\left(\frac{\partial\gamma}{\partial V}\right)\left(\frac{\partial V}{\partial T}\right) + \gamma\left(\frac{\partial\beta}{\partial T}\right)\right]\frac{dT_{cp}}{df} + \left[\beta\left(\frac{\partial\gamma}{\partial V}\right)\left(\frac{\partial V}{\partial f}\right) + \gamma\left(\frac{\partial\beta}{\partial f}\right)\right]. \tag{15}$$

The term in Eq. (14) involving the derivative of $(c_1/c_3)-(c_2/c_4)$ has been omitted since its coefficient is zero at $T = T_{cp}$. The quantity β and its two derivatives, $(\partial\beta/\partial T)$ and $(\partial\beta/\partial f)$ can be found from Eqs. (10), (14), and (15). Table I gives the pertinent data required for these calculations. The subscript cp here signifies "at the temperature T_{cp}." In all cases the values tabulated are at or near T_{cp}. The value of V and $(\partial V/\partial T)$ are taken from x-ray data[7] taken in the cubic phase of solid solution powders.

Table II shows the values of β, $(\partial\beta/\partial f)$, and $(\partial\beta/\partial T)$ calculated from Eqs. (10), (14), and (15) and the data given in Table I. These results are discussed in detail in the next section.

V. DISCUSSION OF RESULTS

Earlier theoretical investigations of the source of the Curie-Weiss behavior in BaTiO$_3$ have been directed toward explaining Eq. (14) in some form or other. Actually only the second term in the brackets was considered, the first term either being ignored or assumed to be zero. Basically, in the earlier work, it was assumed that the primary source of the observed Curie-Weiss law was the statistical mechanical effect of temperature on the effective ionic polarizability of an array of charged particles coupled by dipole fields. In an actual experimental determination of the variation of dielectric constant with temperature, three separate driving forces are operative:

(1) The variation of α_B because of anharmonic terms in the potential energy of the B atom as calculated independently by Slater[3] and Devonshire.[2]

(2) The variation of α_B via changes in interatomic

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[22] Tessman, Kahn, and Shockley, Phys. Rev. **92**, 890 (1953).

spacings as the lattice expands as estimated for $BaTiO_3$ by Devonshire[2] and more recently by this author[4] using the better experimental data that has become available.

(3) The variation of the effective Lorentz field due to the term in Eq. (14) of the form $\beta(\partial\gamma/\partial V)(\partial V/\partial T)$.

To exhibit these effects Eq. (14) may be rewritten:

$$\frac{A'}{2\pi}\left[\frac{c_1}{c_3}-\frac{c_2}{c_4}\right]=\gamma\left(\frac{\partial\beta}{\partial T}\right)_V+\gamma\left(\frac{\partial\beta}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)+\beta\left(\frac{\partial\gamma}{\partial V}\right)\left(\frac{\partial V}{\partial T}\right). \qquad (14')$$

Granicher and Jakits[20] considered the second term on on the right of Eq. (14′) in the discussion of their Eqs. (III. 17) and (III. 18), but did not take into account that their α was actually $\sum\alpha_i\beta_i$ (in their notation) where the β_i play the role of Lorentz factors. The β_i have a large temperature dependence as can be seen from their Fig. 12 which shows the dependence of β_i on volume (and hence temperature).

The left-hand side of Eq. (14′), which is the experimentally determined quantity except for the factor $(c_1/c_3-c_2/c_4)$, is for $f=0$

$$\frac{A'}{2\pi}\left(\frac{c_1}{c_3}-\frac{c_2}{c_4}\right)=0.7\times10^{-5}\ {}^\circ\mathrm{C}^{-1}. \qquad (14'\mathrm{a})$$

The third term on the right for the same composition is

$$\beta\left(\frac{\partial\gamma}{\partial V}\right)\left(\frac{\partial V}{\partial T}\right)=7.1\times10^{-5}\ {}^\circ\mathrm{C}^{-1}. \qquad (14'\mathrm{b})$$

The first two terms on the right, taken together, constitute the quantity tabulated under $(1/\epsilon_0)(\partial\alpha_B/\partial T)_f$ in Table II except for the factor γ or

$$\gamma\left(\frac{\partial\beta}{\partial T}\right)_f=\gamma\left[\left(\frac{\partial\beta}{\partial T}\right)_{V,f}+\left(\frac{\partial\beta}{\partial V}\right)_{T,f}\left(\frac{\partial V}{\partial T}\right)\right]=-6.4\times10^{-5}\ {}^\circ\mathrm{C}^{-1}. \qquad (16)$$

These results are disturbing in that they show that the experimentally determined quantity, A', results from a small difference between two large quantities and hence is very sensitive to the accuracy of the large quantities involved. This makes a quantitative comparison of theory and experiment difficult. From Eqs. (14′a) and (14′b) it appears that the variation of the effective Lorentz factor with temperature is of the correct sign and an order or magnitude larger than that required to produce the observed variation of the dielectric constant with temperature. Since γ is negative, Eq. (16) requires that the temperature coefficient of ionic polarizability of the B ion be positive rather than negative to arrive at the experimentally determined A'. Does this mean that the theories which have predicted the sign of $(\partial\beta/\partial T)_{V,f}$ to be negative are at variance with experiment? The answer seems to be "No," if results reported by Granicher and Jakits and calculations based on a simple model are taken into account.

TABLE II. Values of β, $\partial\beta/\partial T$, and $\partial\beta/\partial f$ calculated from the data in Table I.

f	$(\partial\beta/\partial T)_f$ (A^3 °C^{-1})	$(\partial\beta/\partial f)_T$ (A^3)	α_B/ϵ_0 (A^3)
0	9.4×10^{-4}	-0.45	14.70
0.2	6.7×10^{-4}	-0.40	14.53
0.4	5.3×10^{-4}	-0.40	14.38
0.6	3.6×10^{-4}	-0.51	14.24
0.8	2.8×10^{-4}	-0.59	14.10

In Eq. (16) consider the contribution of the term $(\partial\beta/\partial V)_{T,f}(\partial V/\partial T)$. The magnitude of $(\partial\beta/\partial V)$ can be estimated as follows: Assuming that the lattice is in equilibrium principally under Coulomb and short-range repulsive forces, it can be shown simply that the harmonic part of the potential energy of the B atom against small motions along the polarization axis arises largely from the short range repulsive force due to neighboring oxygens. The resulting ionic polarizability may be written

$$\beta=\lambda r^{11}, \qquad (17)$$

where λ is a constant and r is the distance between the B ion and the nearest oxygen atoms, and it is assumed that the energy of interaction of the B ion and oxygen varies as r^{-9}. Then

$$\left(\frac{\partial\beta}{\partial V}\right)=\left(\frac{\partial\beta}{\partial r}\right)\left(\frac{\partial V}{\partial r}\right)^{-1}=\frac{11(\beta/r)}{3(V/r)}=\frac{11}{3}\frac{\beta}{V}. \qquad (18)$$

This leads to a result $(\partial\beta/\partial V)=0.84$. A similar calculation for β_{Ti} in $BaTiO_3$ yields a value of 0.55. This compares favorably with results given in Fig. 11 of reference 20, from which the equivalent result for Ti in a variety of titanates is found to be 0.46. Using this model, we find

$$(\partial\beta/\partial V)_{T,f}(\partial V/\partial T)=1.66\times10^{-3}\ \mathrm{A}^3\ {}^\circ\mathrm{C}^{-1}.$$

Then, in order to satisfy Eq. (16), we require

$$(\partial\beta/\partial T)_{V,f}=-0.72\times10^{-3}\ \mathrm{A}^3\ {}^\circ\mathrm{C}^{-1}.$$

To compare orders of magnitude: from Slater's[3] Eqs. (27) and (29), the equivalent quantity for Ti in $BaTiO_3$ calculated from the statistical mechanical model yields

$$\frac{1}{\epsilon_0}\left(\frac{\partial\alpha_{\mathrm{Ti}}}{\partial T}\right)_V=-1.0\times10^{-3}\ {}^\circ\mathrm{C}^{-1},$$

if the values of b_1, b_2, and a in Slater's equation (29) are taken from this author's results for $BaTiO_3$ listed in Table III of reference 4.

A similar analysis may be applied to Eq. (15). The first term on the right is found from Eq. (14) and the experimental value of (dT_{cp}/df). Equations (14) and (15) may be combined to write

$$\frac{A'}{2\pi}\left(\frac{c_1}{c_3}-\frac{c_2}{c_4}\right)\left(\frac{dT_{cp}}{df}\right)=-\beta\left(\frac{\partial\gamma}{\partial V}\right)\left(\frac{\partial V}{\partial f}\right)-\gamma\left(\frac{\partial\beta}{\partial f}\right). \quad (19)$$

For $f=0$ (pure $KNbO_3$) the left-hand side of Eq. (19) is -0.34×10^{-2} and the first term on the right is 2.7×10^{-2}. Again if we write

$$\left(\frac{\partial\beta}{\partial f}\right)_T=\left(\frac{\partial\beta}{\partial V}\right)_T\left(\frac{\partial V}{\partial f}\right)_T+\left(\frac{\partial\beta}{\partial f}\right)_{V,T}, \quad (20)$$

and insert the value of $(\partial V/\partial f)_T$ from Table I and $(\partial\beta/\partial V)$ from Eq. (17) the result is $(\partial\beta/\partial f)_{V,T}$ is $\sim+0.2$. This infers that β_{Ta} is 1.4% larger than $\beta_{\mathrm{Nb}}$for fixed volume and temperature. The value of $(\partial\beta/\partial f)_T$ from Table II is -0.45. The effect of f on the volume of the unit cell overrides the variation of β caused by the substitution of Ta for Nb. We are really saying that if a Ta atom replaces an Nb atom, the effective total polarizability would go up, were it not for the fact that the cell volume decreases. Actually this is not unexpected, since the space then occupied by the Ta atom would be too large, which naturally leads to an enhanced ionic polarizability.

VI. SUMMARY AND CONCLUSIONS

Results of measurements of dielectric constants in the paraelectric state of solid-solution single crystals of $KNbO_3$ and $KTaO_3$ have been compared with calculations derived from Slater's model and the assumption of an average polarizability of the atoms occupying the (Nb,Ta) site. It is found that the behavior of the dielectric constant as the concentration in the solid (f) or the temperature (T) is varied can be understood by considering three major effects:

(1) The variation of the effective Lorentz corrections as the volume changes.

(2) The variation of the ionic polarizability as the volume changes.

(3) The variation of the contribution of anharmonic vibrations to the ionic polarizability as either the temperature or composition is changed.

In the system reported on here (1) and (2) have large effects on the dielectric constant but are opposite in sign. Quantitative results on (3), which was the motivation for some earlier theoretical work, are largely obscured by this fact. It is not clear at this stage why these former two large effects do not lead to a situation in some of the ABO_3 perovskites in which the dielectric constant increases with temperature in a paraelectric phase rather than decreases. It may very well be that a direct relation exists between the two volume effects which leads to the observed behavior.

The important new piece of information derived from these investigations is that the Lorentz correction is very dependent on the volume of the unit cell. This work has also suggested that perhaps a better choice for study of solid-solution behavior is the $BaTiO_3$-$SrTiO_3$ system. The reason becomes obvious if we compare (c_4/c_3) calculated for a given volume but for different α_A (polarizability of the atom in the A site). For example, for $\alpha_A/\epsilon_0=24.4(\mathrm{Ba}^{++})$, $c_4/c_3=4.496$, while for $\alpha_A/\epsilon_0=16.8(\mathrm{K}^+)$, $c_4/c_3=4.494$ at $V=64$ A^3. If the model used here is reasonably correct, then the concentration of $SrTiO_3$ should affect the dielectric behavior only via the change in volume of the unit cell. This problem is under study.

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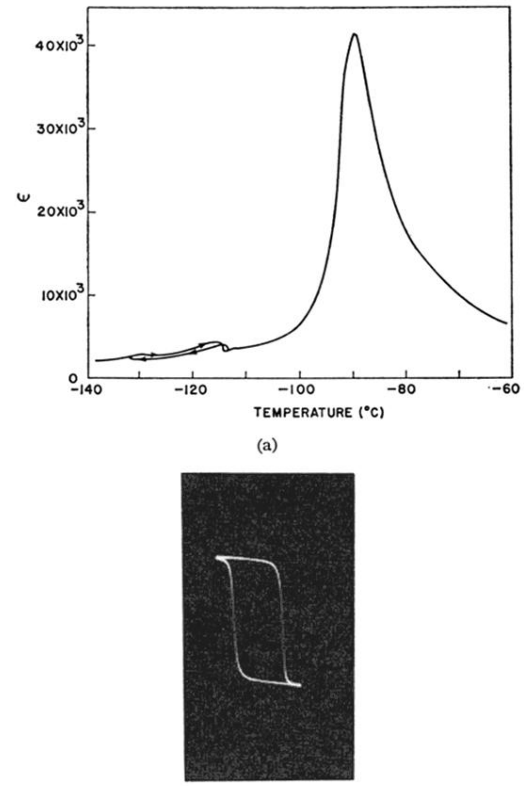

(a)

(b)

FIG. 6. (a) Dielectric constant *vs* temperature in $KTa_{0.8}Nb_{0.2}O_3$. Crystal is plate 0.17 cm×0.095 cm×0.016 cm thick, completely electroded on faces. (b) is oscilloscope trace of 60-cps sine wave hysteresis loop at −167°C; spontaneous polarization is 9.7 μcoul/cm² and coercive field is 0.6 kv/cm.