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Thermodynamics of an eight-site order-disorder model for ferroelectrics

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Thermodynamical properties of an order-disorder model of ferroelectrics proposed by Comes, Lambert, and Guinier for the perovskites $BaTiO_3$ and $KNbO_3$, are discussed. It is shown that in the absence of crystalline distortion induced by the motion of the tunneling ion, the only stable ordered phase is that of symmetry C_{3v}. The ferroelectric-paraelectric transition is a "supersingular" point where the paraelectric phase coexists with three ferroelectric phases. The lattice distortion breaks this degeneracy; unless the distortion is too drastic the system then shows three ferroelectric phases of symmetries C_{3v}, C_{2v}, and C_{4v}, appearing in this order for increasing temperature, in complete agreement with $BaTiO_3$ and $KNbO_3$. The calculated entropy changes associated to the phase transformations are consistently larger than the measured values, showing that a correlation between the configurations of neighboring cells is an essential feature of the model.

I. INTRODUCTION

In this paper we investigate the thermodynamics of a model of ferroelectrics in which one ion can occupy eight equivalent sites at the vertices of a cube. This model has been proposed previously to at least two classes of compounds: the perovskites $BaTiO_3$ and $KNbO_3$ and the isostructural compounds Na_3HfF_7, Na_3ZrF_7, and Na_3UF_7.

A disorder model was proposed for $BaTiO_3$ by Mason and Mathias,[1] in which the Ti can occupy six positions at the vertices of an octahedron. Their model predicts a symmetry C_{4v} for $BaTiO_3$ at 0 °K and was discarded since the compound shows two phases, of symmetry C_{2v} and C_{3v}, below the C_{4v} phase. However, the motion of the Ti continues to be a challenge. Megaw[2] recognized from x-ray diffraction observations that the ions Ba^{+2}, Ti^{+4}, and O^{-3} do not make a well-packed structure, leaving some empty space within which the Ti may move. The point of dispute is whether the potential for the Ti motion is a shallow surface with the minimum at the center of the cell or it has several minima at equivalent positions displaced from the center. $BaTiO_3$ and $KNbO_3$ show a number of anomalies that can be explained, at least qualitatively, by both hypotheses. One of those anomalies is the occurrence of a markedly anisotropic diffuse scattering observed for x rays[3–5] and electrons.[6] Comes *et al.*[5] proposed that the Ti (Nb) ion is located at one of the eight positions shifted from the center along the body diagonals of the cell. The unit cell proposed by those authors is shown in Fig. 1. Cochran,[7] Hüller,[8] and Harada *et al.*[9] have argued that the diffuse scattering can also be explained by the "*soft*" overdamped mode existent in those crystals. This is obviously true as the model proposed by Comes *et al.* predicts, with some details, the existence of the overdamped phonons utilized by Cochran, Hüller, and Harada *et al.* to explain the diffuse scattering. In fact, in the cubic phase all the eight sites of Fig. 1 are equally populated and consequently the Ti "*tunnels*" in the three directions with equal probabilities. This results in an extreme damping for one of the F_{1u} modes, that in which the Ti moves against all the other atoms of the cell. In the tetragonal phase the Ti is preferentially at the faces numbered 1–4 and then *tunnels* on the *xy* plane. Consequently, the damping is much larger for the E component (motion on the xy plane) of F_{1u} than for the A_1 component (motion along z); this makes the E mode overdamped and the A_1 mode underdamped, although perhaps highly damped. Approaching the transition

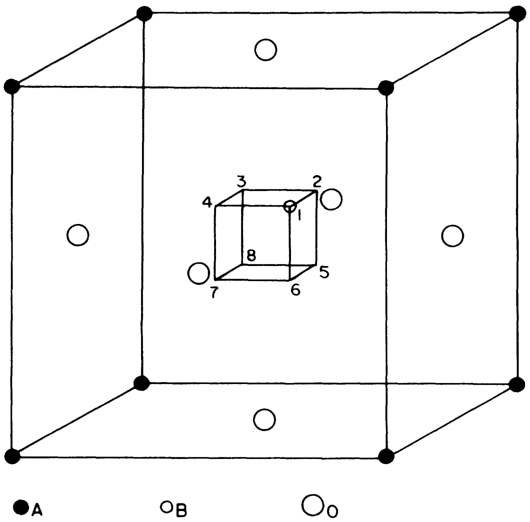

FIG. 1. Unit cell of the perovskites $BaTiO_3$ and $KNbO_3$ as proposed by Comes *et al.*

to the cubic phase the polarization becomes smaller, which implies that the tunneling along z increases; this should result in an increase of the damping of the A_1 mode. Scalabrim *et al.*[10] have shown that the damping of one of the A_1 modes of the tetragonal phase of $BaTiO_3$ increases critically when the cubic phase is approached. In the orthorhombic phase the Ti is preferentially at the sites 1 and 2, and then the tunneling is along x. This makes the B_1 mode overdamped, and the B_2 and A modes underdamped. Finally, in the rhombohedral phase the Ti is preferentially at the site 1 and the modes are underdamped. Summing up, the hypothesis of Comes *et al.* offers a unified explanation of the large-amplitude atomic motion which causes the x-ray anomaly in $BaTiO_3$ and $KNbO_3$, and one should not discard their model without offering another explanation.

The compounds Na_3HfF_7, Na_3ZrF_7, and Na_3UF_7 have a disorder mechanism[11–13] similar to the model of Comes *et al.* The seven atoms of fluorine have eight positions around the Hf (Zr, U) to occupy, so that one of the sites is instantaneously empty. Measurements using x-ray diffraction, differential thermal analysis, and γ-γ angular correlation made by Sette-Câmara[14] and Oliveira[15] on Na_3HfF_7 show that the compound has one order-disorder phase transition at about 430 °K. In contrast with $BaTiO_3$ and $KNbO_3$, Na_3HfF_7 did not show any lattice distortion at the phase transition.

In this paper we show that the ordered phases corresponding to the three symmetries allowed by the model by Comes *et al.* are thermodynamically possible if the lattice has some distortion, and that, when the crystal is cooled, they are expected to appear exactly in the same order observed experimentally. If the lattice has no distortion the only ordered stable phase is that of symmetry C_{3v}. The results of the present calculations are similar to those obtained phenomenologically by Devonshire.[16]

II. THEORY

Define n_i as the occupation probability for the site i. The energy per unit cell of the dipole system, expanded to second order in n_i is

$$\begin{aligned}U = &-\tfrac{1}{2}A(n_1-n_8)^2-\tfrac{1}{2}A(n_2-n_7)^2-\tfrac{1}{2}A(n_3-n_6)^2-\tfrac{1}{2}A(n_4-n_5)^2+\tfrac{1}{6}A(n_1-n_8)[(n_3-n_6)+(n_5-n_4)+(n_7-n_2)]\\ &+\tfrac{1}{6}A(n_2-n_7)[(n_4-n_5)+(n_6-n_3)+(n_8-n_1)]+\tfrac{1}{6}A(n_3-n_6)[(n_1-n_8)+(n_5-n_4)+(n_7-n_2)]\\ &+\tfrac{1}{6}A(n_4-n_5)[(n_2-n_7)+(n_6-n_3)+(n_8-n_1)]\ .\end{aligned}\tag{1a}$$

This formula can be checked with the verification that $-\partial U/\partial n_i$ is proportional to the polarization component pointing to the site i. Formula (1a) can be reduced to

$$\begin{aligned}U = &-\tfrac{1}{3}A\sum_{i=1}^{8}(n_i-n_{9-i})^2\\ &+\tfrac{1}{6}A\left(\sum_{i=1}^{8}(-)^i n_i\right)^2\ .\end{aligned}\tag{1b}$$

When writing the expressions (1) we have considered the potential for the ion's motion to be cubic for all temperatures. We have also neglected thermal expansion, treating the parameter A as temperature independent.

The Helmholtz free energy per cell is

$$F = U - TS = U + kT\sum_i n_i \ln n_i\ .\tag{2}$$

Neglecting the changes in the volume of the unit cell, the Gibbs and Helmholtz functions have equivalent properties, so that F plays the role of the full thermodynamic potential.

As discussed by Comes *et al.* one can make four different arrangements with the occupation numbers n_i, (corresponding to) the symmetries C_{3v}, C_{2v}, C_{4v}, and O_h. In the C_{3v} symmetry configuration we have

$$n_2 = n_4 = n_6\ ,$$

$$n_3 = n_5 = n_7\ ,$$

and the free energy simplifies to

$$\begin{aligned}F = &-\tfrac{1}{2}A[(n_1-n_8)+(n_2-n_7)]^2 + kTn_1\ln n_1\\ &+kTn_8\ln n_8 + 3kTn_2\ln n_2 + 3kTn_7\ln n_7\ .\end{aligned}\tag{3}$$

In the C_{2v} symmetry configuration

$$n_1 = n_2\ ,$$

$$n_7 = n_8\ ,$$

$$n_3 = n_4 = n_5 = n_6\ ,$$

and

$$\begin{aligned}F = &-\tfrac{4}{3}A(n_1-n_8)^2 + 2kTn_1\ln n_1\\ &+2kTn_8\ln n_8 + 4kTn_3\ln n_3\ .\end{aligned}\tag{4}$$

In the C_{4v} symmetry configuration

$$n_1 = n_2 = n_3 = n_4\ ,$$

$$n_5 = n_6 = n_7 = n_8\ ,$$

and

$$F = -\tfrac{8}{3}A(n_1-n_8)^2 + 4kTn_1\ln n_1 + 4kTn_8\ln n_8\ .\tag{5}$$

Finally, in the O_h symmetry configuration

$$n_i = \tfrac{1}{8}, \quad i = 1,\ 2,\ \ldots 8$$

and

$$F = -kT\ln 8 \ . \tag{6}$$

In formulas (3)–(6), we have neglected the contribution to the entropy which comes from the multiplicity of possible arrangements with the same symmetry. If the crystal has N cells, the contributions per unit cell, respectively, for the symmetries C_{3v}, C_{2v}, and C_{4v} are $(k\ln 8)/N$, $(k\ln 12)/N$, and $(k\ln 6)/N$; for large N, this is not significant.

Each different configuration free energy written above has a minimum in the space of coordinates n_i. This minimum generates a branch for the multivalued function $F(T)$. At each temperature the system selects the configuration which corresponds to the lowest branch. We now proceed to the calculation of the various branches of $F(T)$.

A. C_{3v} symmetry configuration

The minimization of the free energy is subject to a normalization constraint

$$n_1 + n_8 + 3n_2 + 3n_7 = 1 \ . \tag{7}$$

In the minimization procedure there are then three independent variables. Taking n_2 as the dependent variable we obtain the relationships

$$\frac{\partial F}{\partial n_1} = -\frac{\partial F}{\partial n_2}\frac{\partial n_2}{\partial n_1} = \frac{1}{3}\frac{\partial F}{\partial n_2} \ , \tag{8}$$

$$\frac{\partial F}{\partial n_8} = \frac{1}{3}\frac{\partial F}{\partial n_2} \ , \tag{9}$$

and

$$\frac{\partial F}{\partial n_7} = \frac{\partial F}{\partial n_2} \ . \tag{10}$$

Dividing (9) by (8) we obtain, after some manipulation,

$$n_2^3 = n_1^2 n_8 \ . \tag{11}$$

Inserting now the relation (10) in (8) and (9),

$$\frac{\partial F}{\partial n_1} = \frac{1}{3}\frac{\partial F}{\partial n_7} \ , \tag{12}$$

$$\frac{\partial F}{\partial n_8} = \frac{1}{3}\frac{\partial F}{\partial n_7} \ . \tag{13}$$

Dividing (12) by (13) we obtain, analogously,

$$n_7^3 = n_1 n_8^2 \ . \tag{14}$$

Using the relations (11) and (14), the normalization condition becomes

$$n_1^{1/3} + n_8^{1/3} = 1 \ . \tag{7'}$$

Defining

$$x_3 = n_1^{1/3} \ ,$$

$$y_3 = n_8^{1/3} \ ,$$

the free energy takes the form

$$F = -\tfrac{1}{2}A(x_3 - y_3)^2 + 3kT(x_3\ln x_3 + y_3\ln y_3) \ . \tag{15}$$

B. C_{2v} symmetry configuration

With an analogous method we obtain

$$n_3^2 = n_1 n_8 \tag{16}$$

and

$$n_1^{1/2} + n_8^{1/2} = \tfrac{1}{2}\sqrt{2} \ . \tag{17}$$

Defining

$$(2n_1)^{1/2} = x_2 \ ,$$

$$(2n_8)^{1/2} = y_2 \ ,$$

the free energy becomes

$$F = -\tfrac{1}{3}A(x_2 - y_2)^2 + 2kT(x_2\ln x_2 + y_2\ln y_2) - kT\ln 2 \ . \tag{18}$$

C. C_{2v} symmetry configuration

$$4n_1 + 4n_8 = 1 \ . \tag{19}$$

Defining

$$4n_1 = x_4 \ ,$$

$$4n_8 = y_4 \ ,$$

we have

$$F = -\tfrac{1}{6}A(x_4 - y_4)^2 + kT(x_4\ln x_4 + y_4\ln y_4) - 2kT\ln 2 \ . \tag{20}$$

Finally, we can write the general formula for the free energy as a function of one single-order parameter, defining

$$x_i = \tfrac{1}{2}(1 + \eta_i) \ ,$$

$$y_i = \tfrac{1}{2}(1 - \eta_i) \ ,$$

$$-1 \le \eta_i \le 1 \ .$$

The free energy can now be expressed as

$$F = -\alpha_0^i\tfrac{1}{6}A\eta_i^2 + \beta_0^i kT\left[\tfrac{1}{2}(1+\eta_i)\ln\tfrac{1}{2}(1+\eta_i) + \tfrac{1}{2}(1-\eta_i)\ln\tfrac{1}{2}(1-\eta_i)\right] - \gamma_0^i kT\ln 2 \ . \tag{21}$$

The parameters α_0, β_0, and γ_0 are pure numbers that depend on the symmetry. Their values are given in Table I.

The parameter η adopts the value η_0 which minimizes F:

$$\left(\frac{\partial F_i}{\partial \eta_i}\right)_{\eta_0^i} = 0 \tag{22a}$$

or

$$\eta_0^i = \tanh(\alpha_0^i A\eta_0^i / 3\beta_0^i kT) \ . \tag{22b}$$

TABLE I. Values of the parameters α_0, β_0, and γ_0 of formula (21) for the various symmetries.

	α_0	β_0	γ_0
C_{3v}	3	3	0
C_{2v}	2	2	1
C_{4v}	1	1	2
O_h	0	0	3

This equation allows numerical calculation of $\eta_0(T)$ for each symmetry, and consequently supplies the numerical values of $F(T)$.

III. NUMERICAL RESULTS

As discussed by Mason,[17] Eq. (22b) has a solution different from zero only if

$$\alpha_0^i A/3\beta_0^i kT > 1 \ . \tag{23}$$

Thus, the disorder temperature for each symmetry of the system is

$$T_d = \alpha_0^i A/3\beta_0^i k \ . \tag{24}$$

Since $\alpha_0 = \beta_0$ for all symmetries, T_d is equal to $A/3k$ for all of them.

The function $F(T)$ is shown in Fig. 2. We see from the figure that the system has the symmetry C_{3v} at low temperatures. At the disorder temperature all the branches join at the same point; this means that the point T_d is a supersingularity where the ordered phases of symmetry C_{3v}, C_{2v}, and C_{4v}, and the disordered phase coexist. This degeneracy can be broken, artificially by external field or uniaxial pressure, or spontaneously due to distortions of the potential. For Na_3HfF_7 the degeneracy of the disorder temperature is probably maintained, or poorly resolved, since the data on angular correlation and differential thermal analysis obtained by Sette Câmara and by Oliveira indicate that the compound has only one phase transition.

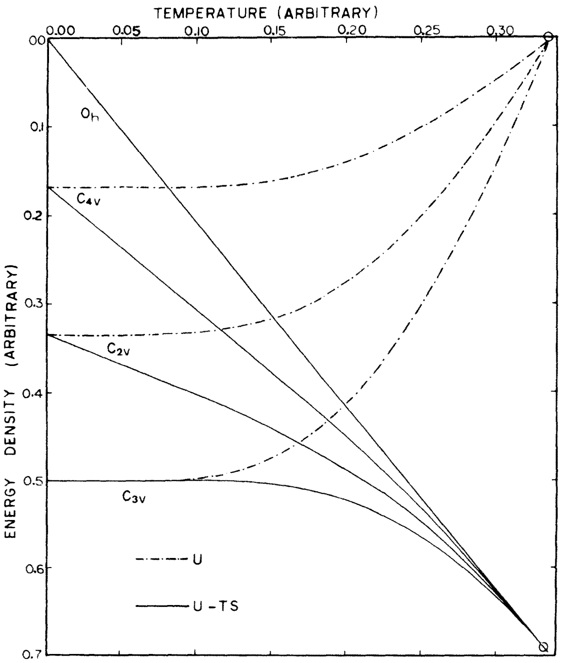

FIG. 2. Densities of internal energy and free energy calculated for an undistorted crystal.

For $BaTiO_3$ and $KNbO_3$ the disorder temperatures are well resolved, and these crystals display all the three ordered phases in the absence of external perturbation. This could result from the distortions that those crystals have in their unit cell for each ordered configuration. The distortion changes the value of the internal energy; however, the expression for the entropy will not be affected. Supposing that after the distortion the internal energy is still proportional to the square of the polarization, the effect of the distortion is to change the value of $\alpha_0 A$.

We define

$$A = 3kT_{C_3} \ .$$

Where T_{C_3} is the disorder temperature for the phase C_{4v}, the effect of the distortion is to change the values of α_0 for the phases C_{2v} and C_{3v}. The corrected values of α_0 (designated by α) can in principle be related numerically to the distortions of the lattice. However, this requires the computation of the potential for the motion of the Ti (Nb) for each shape of the cell. In this paper we calculate the values of α from the measured values of the transition temperatures. The results are shown in Table II. Although the calculated values of the transition temperatures depend on the values of α, the order in which the phases appear is intrinsic of the model: it was found impossible to choose a set of values of α which makes the phases to appear in an order different from $C_{3v} \rightarrow C_{2v} \rightarrow C_{4v} \rightarrow O_h$. The values of α obtained for $BaTiO_3$ and $KNbO_3$ are almost equal. This resulted from the fact that their three transition temperatures, excluding a scale factor which depends only on the parameter A, are very similar. The similarities of the parameters α of $BaTiO_3$ and $KNbO_3$ should also be expected since the distortions of the unit cell for the two materials, in

TABLE II. Adjusted values of α_0 (designated by α) for the ordered phases of $BaTiO_3$ and $KNbO_3$.

	C_{3v}	C_{2v}	C_{4v}
$BaTiO_3$	2.38	1.80	1
$KNbO_3$	2.29	1.80	1

the ordered phases, are analogous.[18,19] On the other hand, the x-ray experiments[14,15] did not show any distortion in the lattice of Na_3HfF_7 around the phase transition.

The adjusted function $F(T)$ for $BaTiO_3$ is plotted in Fig. 3. The function $F(T)$ for $KNbO_3$ is very similar to Fig. 3. From the figure one predicts that these compounds have a first-order transition from the rhombohedral to the orthorhombic phase, another first-order transition from the orthorhombic to the tetragonal phase, and a second-order transition from the tetragonal to the cubic phase. This is in agreement with the experimental evidence about the two lowest transitions. However, the experiments show that the upper transition, in both crystals, is a first-order, or else, a very critical second-order transition.

With the calculated energies we can obtain the entropy changes associated to each transition, from the definition

$$S_i = \Delta Q_i / T_{C_i} \; . \tag{25}$$

The calculated and measured entropies[21–26] are given in Table III. The calculated values are consistently larger than the measured ones. This, in fact, could be predicted by considering one aspect of the model by Comes *et al.*, the occurrence of chains of cells with the same configuration. Those authors included in their model a strong correlation of the instantaneous cell's configuration, along one of the [100] directions. The number n of correlated cells is between 10 and 25. As Lambert and Comes[20] pointed out, this correlation makes the entropy changes n times smaller than the values calculated from the model using independent cells. Following their reasoning, since the x-ray observations indicate that the number n is sample dependent, the measurements of latent heat made on different samples should be in poor mutual agreement. Table III shows large dispersion of the measurements. By comparison between the calculated and measured values of ΔS_i we deduce that $6 < n < 21$ for $BaTiO_3$ and $3 < n < 8$ for $KNbO_3$. This is in reasonable agreement with the values $10 < n < 25$ obtained from x-ray measurements.

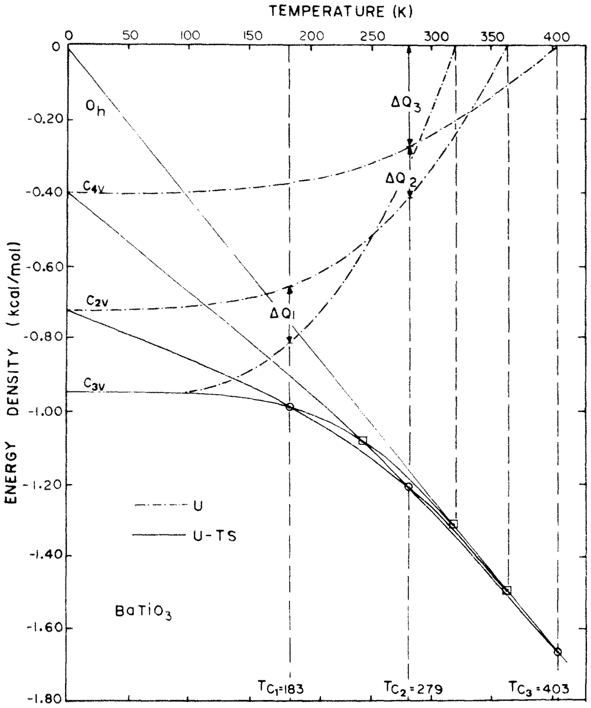

FIG. 3. Densities of internal energy and free energy calculated for $BaTiO_3$.

TABLE III. Entropy changes resulting from the phase transitions of $BaTiO_3$ and $KNbO_3$. ΔS_1 is related to the lowest transition and ΔS_2 is related to the middle one. η is the ratio between the calculated and the measured values.

		Calculated	Measured	η	Reference
	ΔS_1		0.04	21	21
	(cal/mol °K)	0.85	0.07	12	22
			0.06	14	23
			0.076	6.1	21
$BaTiO_3$	ΔS_2	0.47	0.054	8.7	22
			0.058	8.1	23
			0.125	5.6	21
	ΔS_3	0.70	0.12	5.8	22
			0.12	5.8	24
	ΔS_1	0.95	0.12	7.9	25
	ΔS_2	0.47	0.17	2.8	25
$KNbO_3$	ΔS_3	0.70	0.28	2.5	25
			0.19	3.7	26

Since the displacement of the tunneling ion is small compared with the size of the unit cell, we write the field at the ion as

$$\epsilon = E + (\alpha/\alpha_0)(P/3\epsilon_{\parallel}) = (\alpha/\alpha_0)(P/3\epsilon_{\parallel}) \; . \tag{26}$$

In this formula $\epsilon_{\parallel}$ is the component of the dielectric constant along the polarization direction, for frequencies above the typical relaxation frequency of the dipoles; in other words, the component of the dielectric constant created by the electrons and phonons. From (26) we have

$$U = -(\alpha/\alpha_0)(P^2/6\epsilon_{\parallel}) \; . \tag{27}$$

Comparing (27) with formula (21) and Table I we conclude that the component of the polarization along one of the cubic axes of the crystal, for all phases, is given by

$$p^2 = \epsilon_{\parallel} A \eta^2 \; . \tag{28}$$

This is the polarization in molar units; to convert

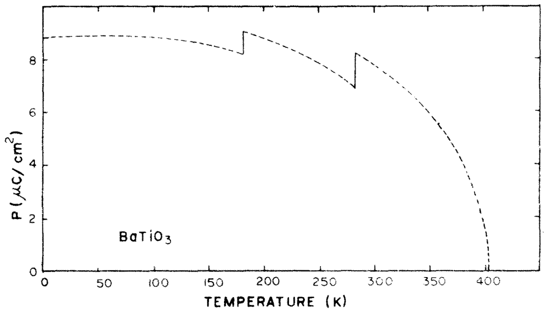

FIG. 4. Spontaneous polarization calculated for $\mathrm{BatiO_3}$. The curve for $\mathrm{KnbO_3}$ has a very similar shape.

this to units of cm^{-3} we have to take the correlation of the cells into account, for this makes the volume of one mole n times larger than the conventional one. The result is

$$p = 4.8(\chi_{\parallel}/n)^{1/2}\eta\ \mu\mathrm{C/cm^2} \tag{29a}$$

for $\mathrm{BaTiO_3}$ and

$$p = 6.4(\chi_{\parallel}/n)^{1/2}\eta\ \mu\mathrm{C/cm^2} \tag{29b}$$

for $\mathrm{KNbO_3}$. In the formula above $\chi_{\parallel}$ is the relative susceptibility $\epsilon_{\parallel}/\epsilon_0$.

The experimental information about $\chi_{\parallel}$ is incomplete. For $\mathrm{BaTiO_3}$ in the tetragonal phase Burns[27] found that $\chi_{\parallel}$ varies from 32 to 45. Scalabrin *et al.* used a more accurate method to determine $\chi_{\parallel}$ and found that it is equal to 30 for all temperatures in the tetragonal phase. We calculate p supposing $\chi_{\parallel} = 30$ and $n = 10$ for all phases. The result is shown in Fig. 4. The shape of the curve has a reasonable resemblance with the results of measurements and the saturation polarization is about half the measured values.[28–30]

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[1] W. P. Mason and B. T. Matthias, Phys. Rev. 74, 1622 (1948).

[2] H. D. Megaw, Trans. Faraday Soc. 42A, 224 (1946).

[3] M. Lambert, A. M. Quittet, and C. Taupin, Acta Crystallogr. 16, 52 (1963).

[4] J. Harada and G. Honjo, J. Phys. Soc. Jpn. 22, 45 (1967).

[5] R. Comes, M. Lambert, and A. Guinier, Solid State Commun. 6, 715 (1968).

[6] G. Honjo, S. Kodera, and N. Kitamura, J. Phys. Soc. Jpn. 19, 351 (1964).

[7] W. Cochran, Phys. Status Solidi 30, *K*157 (1968).

[8] A. Hüller, Solid State Commun. 7, 587 (1969).

[9] J. Harada, J. D. Axe, and G. Shirane, Phys. Rev. B 4, 155 (1971).

[10] A. Scalabrin, Ph.D. dissertation(University of Southern California, 1974) (unpublished); A. Scalabrin, A. S. Chaves, and S. P. S. Porto (unpublished).

[11] W. H. Zachariasen, Acta Crystallogr. 1, 265 (1948).

[12] L. A. Larris, Acta Crystallogr. 12, 172 (1959).

[13] E. Gerdau, B. Scharnberg, and H. Winkler, in Proceedings of the International Conference on Hyperfine Interactions detected by Nuclear Radiation, Rchovot-Israel, 1970 (unpublished); *Hyperfine Interactions in Excited Nucleus* (Gordon and Breach, New York, 1971), Vol. 3, p. 861.

[14] A. D. R. Sette Câmara, thesis (University de Grenoble, France, 1971) (unpublished).

[15] A. L. Oliveira, MS dissertation (Universidade Fed. Minas Gerais, Brasil, 1974) (unpublished).

[16] A. F. Devonshire, Philos. Mag. 40, 1040 (1949); 42, 1065 (1951).

[17] W. P. Mason, Phys. Rev. 72, 854 (1947).

[18] H. E. Kay and P. Vousdin, Philos. Mag. 40, 1019 (1949).

[19] G. Shirane, R. E. Nawnham, and R. Pepinsky, Phys. Rev. 95, 581 (1954).

[20] M. Lambert and R. Comes, Solid State Commun. 7, 305 (1969).

[21] G. Shirane and A. Takeda, J. Phys. Soc. Jpn. 7, 1 (1952).

[22] J. Wolger, Philos. Res. Rep. 7, 21 (1952).

[23] S. S. Todd and R. E. Lorenson, J. Am. Chem. Soc. 74, 2043 (1952).

[24] H. Blattner and W. Merz, Helv. Phys. Acta 21, 210 (1948).

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

[26] S. Tricbwasser and J. Halpern, Phys. Rev. 98, 1562 (1955).

[27] G. Burns, Phys. Lett. A 43, 271 (1972).

[28] W. J. Merz, Phys. Rev. 76, 1221 (1949); 91, 513 (1953).

[29] H. H. Wieher, Phys. Rev. 99, 1161 (1955).

[30] S. H. Wemple, M. Didomenico, Jr., and I. Camlibel, J. Phys. Chem. Solids 28, 1797 (1968).