were found in the room-temperature structure of $PbTiO_3$.[3] Particularly these short Pb—O bonds, in $PbZrO_3$ as well as in $PbTiO_3$, indicate that the homopolar bond system plays an important role. Megaw[23] predicted that in $PbZrO_3$ the same pyramidal environment of Pb should be achieved which obtains in tetragonal PbO, where the Pb—O bonds form a flat tetragonal pyramid with Pb at the apex. Such a pyramidal environment was, in fact, found in the room-temperature structure of ferroelectric $PbTiO_3$,[3] but does not occur in $PbZrO_3$. In the latter, if we need such a model at all, the shortest Pb—O bonds rather form a flat triangular pyramid with Pb at the apex. The distance between the oxygens at the corner of such a pyramid are 2.89 A, 2.88 A, and 2.75 A. The direction of the normal from the Pb atom to the plane of these three oxygens is approximately that of the [111] direction in the original cubic lattice; this may be related to the fact that a strong electric field induces, in the vicinity of the transition temperature, a ferroelectric phase which was proved to be rhombohedral.[21] It would also be interesting to determine whether such a type of pyramidal environment of the Pb atoms occurs in the as yet unknown structure of the orthorhombic modification of PbO.

Tables of Observed and Calculated Intensities and Structure Factors

Three tables of observed and calculated diffraction data have been prepared[24]: Table III: Observed and Calculated Neutron Powder Diffraction Data for $PbZrO_3$. Table IV: $PbZrO_3$: Comparison Between Observed and Calculated Structure Factors F_{hk0}. Table V: $PbZrO_3$: Comparison Between Observed and Calculated Structure Factors $F_{h,2h,l}$.

VII. ACKNOWLEDGMENTS

The authors are grateful to Dr. L. Corliss and Dr. J. Hastings of the Department of Chemistry, Brookhaven National Laboratory, for obtaining the excellent neutron powder data as illustrated in Fig. 4(b).

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

[24] These tables have been deposited as Document No. 5074 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C., U. S. A. A copy may be secured by citing the document number and by remitting \$3.75 for photoprints or \$2.00 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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Neutron Diffraction Study of Orthorhombic $BaTiO_3$†

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The atomic positions of ferroelectric $BaTiO_3$ in its orthorhombic phase have been determined by a single-crystal neutron diffraction analysis. Pillar-shaped crystals with their major axes along the cubic [110] direction were maintained as single domains by the application of an electric field. The structure deduced can be viewed as a framework of slightly distorted oxygen octahedra, in which the central Ti ions are displaced towards one of the octahedron edges (polar axis) by 0.13 A. The Ba ions are also shifted in the same direction but by the smaller amount of 0.07 A. A comparison of this structure with that of the tetragonal phase suggests the essential role of Ti in the ferroelectricity of this crystal as treated by Slater.

I. INTRODUCTION

It is well known that $BaTiO_3$ exhibits three ferroelectric phases.[1,2] Possessing a cubic perovskite structure at high temperatures, $BaTiO_3$ transforms to a tetragonal modification at its Curie temperature around 120°C. Upon further cooling, the symmetry changes to orthorhombic at 5°C and to rhombohedral at $-80°C$. The dielectric anomalies at these transitions, as well as the associated changes in other physical properties, have been well established.

A knowledge of the exact atomic positions in the three phases is of fundamental importance to the understanding of the ferroelectric behavior of $BaTiO_3$. The first steps taken in this direction were the careful x-ray studies of the tetragonal phase carried out by Kaenzig[3] and by Evans.[4] Although the structure of $BaTiO_3$ is very simple, it appeared that reliable information of the atomic positions cannot be given by x-ray analysis. This is a consequence of the small

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† Development supported by Brookhaven National Laboratory, the U. S. Atomic Energy Commission, the Air Force Office of Scientific Research, and the Signal Corps Engineering Laboratory. X-RAC and S-FAC calculations are supported by the Office of Naval Research.

[1] H. F. Kay and P. Vousden, Phil. Mag. 40, 1019 (1949).

[2] P. W. Forsbergh, Jr., Phys. Rev. 76, 1187 (1949).

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

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

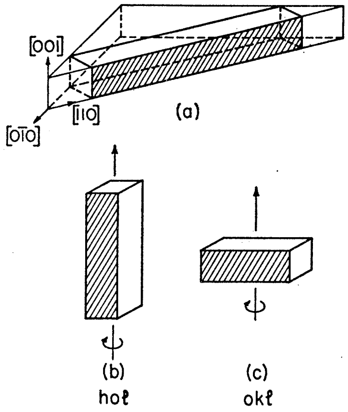

FIG. 1. Crystal orientations used in the study of orthorhombic $BaTiO_3$. Directions in (a) are referred to the cubic axes.

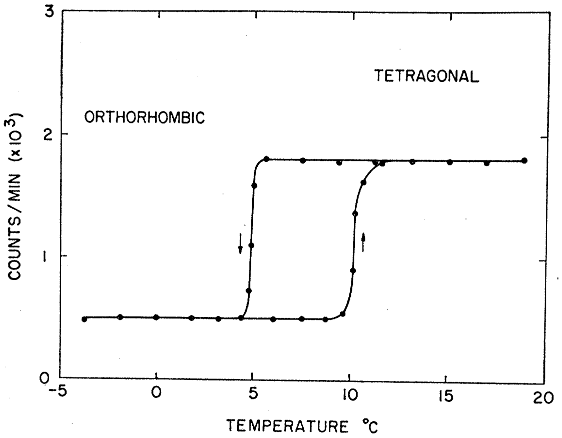

FIG. 2. Temperature dependence of counting rate of (200) reflection. The change is due to a slight reorientation of the crystal at the transition. The counter is set at the peak position at room temperature.

scattering factor of oxygen for x-rays compared with that of Ba. Under these circumstances x-ray methods are insensitive to the small ionic shifts from the cubic positions. However, the difficulty can be removed by employing neutron diffraction techniques, where the oxygen scattering power is of the same order of magnitude as the scattering powers of Ba and Ti. A recent neutron diffraction study by Frazer, Danner, and Pepinsky[5] has established the tetragonal structure unambiguously.

It should be emphasized that neutron diffraction studies of $BaTiO_3$ have been possible only since the method of growing large plate-like single crystals was discovered by Remeika.[6] Even with the flux of 4×10^{12} neutrons/cm^2 sec available at the Brookhaven reactor, relatively large crystals are required to give sufficient intensities. For example, the study of the tetragonal phase was carried out using a single crystal whose dimensions were $12\times3\times0.3$ mm.

In addition, the application of an electric field is necessary to maintain the crystal as a single domain. This is easily done in the tetragonal phase since the major surfaces, the (100) faces, are the ones to be electroded. In the orthorhombic case, however, the field must be applied along the cubic [110] direction, which is the polar direction for this phase. This requires that the crystal plates from which the samples are cut must be relatively thick. Figure 1(a) shows the orientation of the sample with respect to the natural crystal plate.

The crystals used in this study, grown by the Remeika technique, were furnished through the courtesy of Dr. H. Jaffe and Mr. L. Shiozawa of the Clevite Research Center. The purity of the crystals was reported as better than 99.9% and the Curie temperature as between 120°C and 130°C.

II. EXPERIMENTAL

The symmetry of orthorhombic $BaTiO_3$ is that of the space group $Amm2-C_{2v}^{14}$.[1] At −10°C the dimensions of the unit cell are

$$a=3.990\text{ A},\quad b=5.669\text{ A},\quad c=5.682\text{ A},$$

where a coincides with one of the original cube axes, while b and c are rotated 45° with respect to the two remaining cube axes. This unit cell is approximately twice as large as the simple cubic cell, and contains two molecular units. The atomic positions are given as follows:

2 Ba at $(0, 0, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$;
2 Ti at $(\frac{1}{2}, 0, \frac{1}{2}+\delta z_{\mathrm{Ti}})$, $(\frac{1}{2}, \frac{1}{2}, \delta z_{\mathrm{Ti}})$;
2 O_{I} at $(0, 0, \frac{1}{2}+\delta z_{\mathrm{OI}})$, $(0, \frac{1}{2}, \delta z_{\mathrm{OI}})$;
4 O_{II} at $(\frac{1}{2}, \frac{1}{4}+\delta y, \frac{1}{4}+\delta z_{\mathrm{OII}})$, $(\frac{1}{2}, \frac{3}{4}+\delta y, \frac{3}{4}+\delta z_{\mathrm{OII}})$, $(\frac{1}{2}, \frac{3}{4}-\delta y, \frac{1}{4}+\delta z_{\mathrm{OII}})$, $(\frac{1}{2}, \frac{1}{4}-\delta y, \frac{3}{4}+\delta z_{\mathrm{OII}})$.

The four positional parameters, along with the temperature parameters for each nonequivalent atom type, completely determine the structure.

Figures 1(b) and 1(c) illustrate the two types of crystal mounting used for the collection of $(h0l)$ and $(0kl)$ intensity data, respectively. The dimensions of the crystal used for the $(h0l)$ observations were $12\times0.7\times0.7$ mm. A somewhat smaller crystal, of size $4\times0.7\times0.7$ mm, was used to obtain the $(0kl)$ reflections because of the anticipated extinction effects for a crystal in this orientation. Despite its reduced size, the latter crystal had a large enough volume to give measurable intensities for all reflections. In both cases, air-dry silver paint was used to form the electrodes, and a dc biasing field of 10 kv/cm was obtained by placing a 700-volt potential across the crystal.

Several reflections of the $(h0l)$ class were observed at room temperature. The observed integrated intensities, which have (hll) indexing in the tetragonal phase, were in excellent agreement with the calculated intensities based on the reported structure.[5] Upon cooling the crystal, the transition to the orthorhombic phase was clearly indicated by a change in the counting

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[5] Frazer, Danner, and Pepinsky, Phys. Rev. **100**, 745 (1955).
[6] J. P. Remeika, J. Am. Chem. Soc. **76**, 940 (1954).

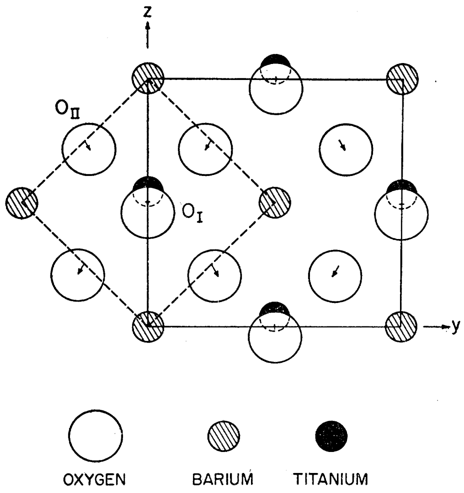

FIG. 3. Projection of orthorhombic $BaTiO_3$ on the (100) plane.

rate of the (200) peak, as shown in Fig. 2. The transition temperature is 5°C on cooling and 10°C on heating.

All intensity data for the orthorhombic phase were collected at $+1$°C. This temperature was attained by using a simple cooling system, in which dry air, after passing through a dry ice bath, was blown over the crystal. A copper-constantan thermocouple was used to indicate the temperature, which was kept constant to within ±0.2°C.

A conventional double-crystal spectrometer, utilizing a monochromatic neutron beam of 1.053 A wavelength from the Brookhaven reactor, was employed to observe all reflections for which $2\theta < 100°$. A total of fifty Bragg reflections, 25 ($h0l$) and 25 ($0kl$), were scanned. The scanning speeds ranged between 1.25 min and 10 min/per 0.1° in 2θ, depending on the intensity. The magnitudes of the observed structure factors, $|F_0|$, were calculated from the integrated intensities by the relation $|F_0| = K(I \sin 2\theta)^{\frac{1}{2}}$, where K is a scale factor.

The structure was determined by the trial and error method. It was clear, at an early stage of the analysis, that extinction effects were negligible except in the strongest reflection, the (102). No effort was made to correct for the extinction effect, and the (102) was omitted in the subsequent analysis. Two groups of reflections, the $(2n+1, 0, 4n)$ and the $(0, 2n+1, 2n+1)$, were quite sensitive to changes in the parameters. The final parameters, determined to give the best agreement for both ($h0l$) and ($0kl$) reflections, were

$$\delta z_{\mathrm{Ti}} = +0.010,$$
$$\delta z_{\mathrm{O_I}} = -0.010,$$
$$\delta z_{\mathrm{O_{II}}} = -0.013, \quad \delta y_{\mathrm{O_{II}}} = +0.003.$$

The values of the scattering lengths used in the above calculations are 0.52, -0.38, and 0.58×10^{-12} cm for Ba, Ti, and O, respectively.[7] The comparison between the observed and the calculated structure factors is shown in Table I. The agreement is excellent, giving a discrepancy factor $R = \sum \big| |F_0| - |F_c| \big| / \sum |F_0|$ of 0.037.

Particular attention was given to the possibility of the existence of other sets of δ's which might give equally good agreement with the observed data. For example, all structures involving combinations of "signs" of δz and δy for O_I and O_{II} were examined. However, none of these models satisfied the observed data.

III. DISCUSSION

The projection of the structure of orthorhombic $BaTiO_3$ on the (100) plane is shown in Fig. 3. With respect to Ba at the origin, the Ti atom is displaced from its "cubic" position by 0.06 A in the positive z direction. The oxygen atoms O_{II}, which are coplanar with the Ti atoms, are shifted by 0.07 A in the opposite direction. In addition, the O_{II} have small shifts in the y direction, such that their resultant displacement is "toward" the Ti atom. The remaining oxygen atoms O_I are displaced in the negative z direction.

Since the choice of origin is arbitrary along the z direction, we can alternately describe the structure in terms of the Ti and Ba atoms with respect to the oxygen octahedra. Choosing the origin such that the shifts of O_{II} atoms in the z directions are zero, Ti and Ba are displaced 0.13 A and 0.07 A, respectively, in the positive z direction. The large Ti displacement may be associated with the slight distortion of the oxygen octahedron in which the O_{II} are shifted 0.02 A parallel

TABLE I. $BaTiO_3$: observed and calculated structure factors, in unit of 10^{-12} cm. Temperature factor B is 0.41 A^2 for ($h0l$) and 0.45 A^2 for ($0kl$).

($h0l$)	$\|F_0\|$	$\|F_c\|$	($0kl$)	$\|F_0\|$	$\|F_c\|$
002	0.88	0.85	020	0.85	0.87
004	3.68	3.64	040	3.66	3.55
006	0.67	0.64	060	0.75	0.75
008	3.17	3.26	080	3.01	2.99
100	0.62	0.64	011	0.66	0.64
102[a]	4.53	5.15	031	0.74	0.68
104	0.99	0.89	051	0.58	0.58
106	4.11	4.38	071	0.65	0.67
108	1.10	1.17	002	0.84	0.85
200	3.87	3.66	022	3.63	3.67
202	0.83	0.83	042	0.81	0.80
204	3.65	3.55	062	3.59	3.29
206	0.66	0.63	013	0.78	0.75
208	3.17	3.18	033	0.59	0.62
300	0.66	0.60	053	0.84	0.80
302	4.64	4.89	004	3.53	3.62
304	0.86	0.84	024	0.77	0.77
306	4.29	4.16	044	3.44	3.42
400	3.39	3.39	015	0.70	0.77
402	0.75	0.76	035	0.83	0.89
404	3.54	3.28	055	0.60	0.59
500	0.64	0.54	006	0.69	0.65
502	4.24	4.41	026	3.35	3.39
504	0.85	0.76	017	0.89	0.93
600	3.23	2.98	008	3.10	3.19

[a] (102) reflection was not used for analysis because of probable extinction effect.

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[7] C. G. Shull and E. O. Wollan, Phys. Rev. **81**, 527 (1951).

to y, resulting in even shorter Ti$-$O$_{\text{II}}$ distances, and the O$_{\text{I}}$ are shifted 0.02 A in the direction of the Ti displacement.

These shifts result in large differences in the bond lengths between Ti and the six surrounding oxygens. The Ti$-$O$_{\text{II}}(+)$ bond becomes 1.90 A, while the remaining Ti$-$O bonds are 2.00 A and 2.10 A as shown in Fig. 4. The shortest bond is somewhat smaller than the sum of the Goldschmidt radii, 1.96 A. On the other hand, the changes in the Ba$-$O and O$-$O bond lengths are small, the former ranging from 2.78 to 2.90 A, while the latter range from 2.80 to 2.87 A.

A comparison of the orthorhombic and tetragonal structures, based on different origins, is given in Table II. The unit cell dimensions and atomic positions for the tetragonal structure are:

$a=3.986$ A, $c=4.026$ A;
Ba $(0, 0, 0)$; Ti $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+0.015)$; O$_{\text{I}}$ $(\frac{1}{2}, \frac{1}{2}, -0.023)$;
O$_{\text{II}}$ $(\frac{1}{2}, 0, \frac{1}{2}-0.014)$, $(0, \frac{1}{2}, \frac{1}{2}-0.014)$.

It should be noted that in the tetragonal phase Ti has one nearest oxygen neighbor (O$_{\text{I}}$) at a distance of 1.86 A, while in the orthohombic phase Ti has two nearest oxygen neighbors (O$_{\text{II}}$) at 1.90 A.

In view of the slight distortion of the oxygen octahedron present in both the tetragonal and orthorhombic structures of BaTiO$_3$, it appears definite that the various models which presupposed a drastic distortion of the oxygen framework may be excluded. In this respect, it may be added that tetragonal PbTiO$_3$ shows little distortion of the O$_6$ group.[8] On the other hand, we can obtain a uniform picture encompassing both the tetragonal and orthorhombic structures if we consider the small distortion of the oxygen octahedron as a result of the displacement of Ti and Ba along the polar axis.

The essential role of Ti is in line with the Slater theory,[9] in which the ferroelectric behavior of BaTiO$_3$ arises because of the Lorentz correction, leading to a vanishing term in the denominator of the expression for the dielectric constant. In his treatment Slater computed the Lorentz correction exactly, taking into account the precise crystal structure. The temperature dependence of the polarizability, which is essential to the phase transition, is assumed to come from a temperature variation of the ionic polarizability of Ti. Although the treatment was limited to the cubic to tetragonal phase change, the same mechanism seems to be of the essential character for the tetragonal to orthorhombic transition.

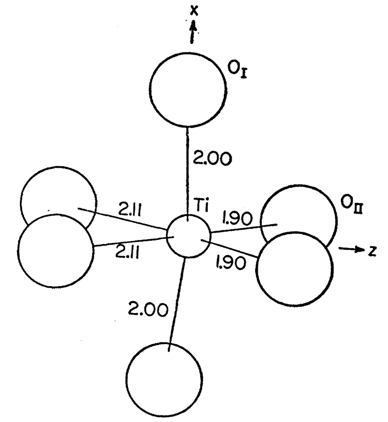

FIG. 4. Environment of Ti in orthorhombic BaTiO$_3$. Interatomic distances given in A.

TABLE II. Comparison of ion shifts in orthorhombic and tetragonal phases, with respect to different origins, for BaTiO$_3$.

		Orthorhombic	Tetragonal
(A) Ba (000)			
δz	Ti	$+0.06$ A	$+0.06$ A
	O$_{\text{I}}$	-0.06 A	-0.09 A
	O$_{\text{II}}$	-0.07 A	-0.06 A
δy_{OII}		± 0.02 A	...
(B) Origin is chosen to give $\delta z_{\text{OII}}=0$.			
δz	Ti	$+0.13$ A	$+0.15$ A
	Ba	$+0.07$ A	$+0.09$ A
	O$_{\text{I}}$	$+0.02$ A	-0.03 A

It is well established experimentally that the behavior of BaTiO$_3$ through the three phase transitions can be explained by the "single" free energy function of Devonshire.[10] This imposes the restriction that any atomistic model proposed to explain the mechanism of the ferroelectric properties of BaTiO$_3$ must satisfy this thermodynamical requirement. A further consequence of the Devonshire theory is that once the proper model has been established in the cubic phase, and if this model can account for the temperature change of free energy in the cubic phase, no further assumptions are needed to account for each phase change.

The observed structure of BaTiO$_3$ in the tetragonal and orthorhombic phases may provide important information concerning the form of the proper atomic model in the cubic phase. For example, according to Devonshire's estimate[10] the oxygen atoms are more loosely bound to their symmetrical positions than are the Ti atoms, provided we assume BaTiO$_3$ to be a purely ionic crystal. This was the basis of the oxygen displacement theory of Jaynes.[11] However the observed structures suggest the essential role of Ti as treated by Slater.

It is certainly possible that besides the long-range dipole interaction considered by Slater, other factors such as the bond character of the constituent atoms play an important role in determining the free-energy function. In this respect, a more satisfactory theoretical treatment is awaited. It is certain now, however, that whatever the origins of ferroelectricity may be, they

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[8] Shirane, Pepinsky, and Frazer, Acta Cryst. **9**, 131 (1955).

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

[10] A. F. Devonshire, Phil. Mag. **40**, 1040 (1949); **42**, 1065 (1951).

[11] E. T. Jaynes, Phys. Rev. **79**, 1008 (1950).

must be physical quantities which are changing gradually and continuously even through the phase transitions. It must be emphasized, therefore, that the observed changes in the Ti—O bonds in $BaTiO_3$ do *not* necessarily imply that a change in the covalent bond system is the "origin" of the ferroelectricity of this crystal, as has been suggested by Megaw.[12]

The essential difficulty of Megaw's theory is not in the fact that she emphasized the covalent bond in the crystal, but in the point that she considered the "abrupt" changes of the bond character at each transition as the origin of the ferroelectricity. On the contrary, the short bond lengths may be a result of the restrictions imposed by the free-energy requirement through the phase change.

The atomic displacement along the polar direction result in a spontaneous polarization. Unfortunately no reliable information about the ionic charges in $BaTiO_3$ has been provided, and it is not likely that $BaTiO_3$ is purely ionic. Nevertheless, the polarization calculated on the assumption of ionic character may provide an estimate of the maximum contribution of the ionic part. The observed ion shifts give 17 microcoulombs/cm in the tetragonal phase at room temperature, and 16 microcoulombs/cm^2 in the orthorhombic phase near 0°C. The observed spontaneous polarizations are 26 and 29 microcoulombs/cm^2, respectively[13,14]; the latter was calculated from the observed value along [100]. The differences between the observed values and the calculated ionic contributions based upon an assumed purely ionic crystal may be considered as an estimate of the minimum contribution to be accounted for by electronic polarization.

In this structure analysis we have assumed the polar direction in the orthorhombic phase to be the cubic [110]. Recently, Berlincourt *et al.*[15] have raised the question that the polar axis might be the cubic [100], rather than [110] as previously accepted. Their argument is based on an extremely high electromechanical coupling coefficient observed along the cubic [100] direction in the orthorhombic phase. Although optical observations by Kay and Vousden[1] and by Forsbergh[2] under the application of an electric field seem to have provided strong evidence for the polar axis to be [110], one more additional dielectric test was carried out in our X-Ray and Crystal Analysis Laboratory with the help of Professor F. Jona. The temperature dependence of the spontaneous polarization was studied with the crystal used for the ($h0l$) neutron observations. With the field applied along the cubic [110] direction, the spontaneous polarization increases by about 40% on cooling through the tetragonal-orthorhombic phase transition. This, combined with the previously reported drop along the [100] direction,[16] can be considered as a sufficient proof that the polar direction is not [100], but is [110] as has been accepted.

We are very grateful to Dr. H. Jaffe and Mr. L. Shiozawa for supplying the single crystals of $BaTiO_3$, and to Professor F. Jona for measurement of the temperature dependence of the spontaneous polarization. We are also grateful to Professor Jona and to Dr. B. C. Frazer for helpful discussions.

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[13] W. J. Merz, Phys. Rev. **91**, 513 (1953).

[14] H. H. Wieder, Phys. Rev. **99**, 1161 (1955).

[15] Berlincourt, Jaffe, and Shiozawa, Bull. Am. Phys. Soc. Ser. II, **1**, 132 (1956).

[16] W. J. Merz, Phys. Rev. **76**, 1221 (1949).