(on the absolute scale) of small **k** values for which the resolution of the neutron scattering technique is usually rather poor. Most hopefully, the effect could be observed in the a direction (near T_0), in which the ferroelectric mode and the longitudinal acoustic mode are polarized perpendicularly to each other. Therefore, arranging the experiment in such a way that only phonons with particular polarization are detected, the neutron inelastic scattering peak from one branch should decrease rapidly near k_0, and the peak from the other branch should increase as the mode polarizaton changes gradually from one to the other. As a result, one could expect to observe near k_0 two fairly close peaks with different intensities. However, because the individual peaks have nonzero widths, certainly comparable with their frequency separation near k_0, one unresolved, markedly asymmetric peak most likely will be observed. (This asymmetry will change drastically with k near k_0.) Similar conclusions about the form of the differential cross section (two peaks or one unresolved asymmetric peak, depending on the damping of modes) can be made[10] if the anharmonic, essentially electrostrictive, interaction (not considered explicitly in this paper) between close mixed branches near k_0 is taken into account. Therefore, to analyze properly the observed form of the cross section, anharmonic effects should be considered explicitly. Anharmonic effects, in general, will also remove the accidental degeneracy of the ferroelectric and acoustic branches in the cubic phase of $BaTiO_3$, in which the piezoelectric effect is missing.

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[10] Yu. Kagan and A. P. Zhernov, Zh. Eksperim. i Teor. Fiz. **48**, 971 (1965) [English transl.: Soviet Phys.—JETP **21**, 646 (1965)].

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Theory of Symmetry Change in Second-Order Phase Transitions in Perovskite Structure*

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An analysis is presented of the compatible subgroups which can arise by second-order phase transition from the perovskite structure, without change of unit cell. The symmetry analysis is based upon the subduction-criterion simplification of the thermodynamic Landau theory. The possible displacements from the perovskite structure are taken as the normal modes at $\mathbf{k}=(0, 0, 0)$. Additional criteria for selecting compatible subgroups are developed, based on a chain of subgroups. Only eight space groups can arise in this manner, of which six can be ferroelectric. An error in the previous theoretical analysis by Haas is eliminated. Our results are compared to the meager experimental determinations of compatible subgroups, but more such determinations are needed.

1. INTRODUCTION AND METHOD

IN the present paper we report on a theoretical analysis carried out in the framework of the thermodynamic Landau[1,2] theory of second-order phase transitions in crystals, to determine the possible lower-symmetry space groups which can arise from the perovskite space group $Pm3m-O_h^1$, without change of unit cell.

The Landau theory[3] assumes the existence of a single thermodynamic potential (e.g., Gibbs or Helmholtz free energy) G which is capable of describing the thermodynamic state of both high- and low-symmetry phases of a solid. By hypothesis, this potential is a function of sets of quantities $c_\alpha^{(\mathbf{k}_\sigma)(m)}$, which are chosen to span an irreducible linear vector space of the high-symmetry space group $\mathfrak{G}_0$. That is, the set

$$\{c_\alpha^{(\mathbf{k}_\sigma)(m)}\} \qquad \alpha=1\cdots l_m, \qquad \sigma=1\cdots s \tag{1}$$

spans the irreducible linear vector space

$$\Sigma^{(\star\mathbf{k})(m)}, \tag{2}$$

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[1] L. D. Landau, Z. Physik **11**, 26 (1937); L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Inc., New York, 1958), Chap. XIV.

[2] C. Ya. Lyubarski, *Application of Group Theory in Physics* (Pergamon Press, Inc., New York, 1960), Chap. XII.

[3] Also reviewed by J. L. Birman, in *Ferroelectricity*, edited by E. F. Weller (American Elsevier Publishing Co., Inc., New York, 1967), pp. 20–61.

so that the potential

$$G(\{c_\alpha^{(\mathbf{k}\sigma)(m)}\}) \tag{3}$$

is a scalar invariant of the group $\mathfrak{G}_0$ when the crystal is in its high-symmetry state, and of the group $\mathfrak{G}_1$ when the crystal is in its low-symmetry state. Then $G(\{c_\alpha^{(\mathbf{k}\sigma)(m)}\})$ may be expanded into a series of scalar invariant, homogeneous polynomials in the $\{c_\alpha^{(\mathbf{k}\sigma)(m)}\}$:

$$G=G^{(0)}+G^{(1)}+G^{(2)}+\cdots G^{(s)}+\cdots, \tag{4}$$

where $G^{(s)}$ is of sth degree. Consonant with this theory, it suffices to work with the quantities $\{c_\alpha^{(\mathbf{k}\sigma)(m)}\}$, which span a *single* space-group irreducible representation, $\mathfrak{D}^{(\star\mathbf{k})(m)}$. On the other hand, the density function $\rho(\mathbf{r})$, also capable of describing high- and low-symmetry phases, can be written

$$\rho(\mathbf{r})=\rho_0(\mathbf{r})+\delta\rho(\mathbf{r}), \tag{5}$$

where $\delta\rho(\mathbf{r})$ is a *linear* function of the $\{c_\alpha^{(\mathbf{k}\sigma)(m)}\}$:

$$\delta\rho(\mathbf{r})=\sum_{\alpha\sigma} c_\alpha^{(\mathbf{k}\sigma)(m)}\psi_\alpha^{(\mathbf{k}\sigma)(m)}(\mathbf{r}). \tag{6}$$

The symmetry group $\mathfrak{G}$ of the crystal is the set of all space-group operations $\{\phi \mid \mathbf{t}\}$ such that $\rho(\mathbf{r})$ is invariant under $\{\phi \mid \mathbf{t}\}$.

The thermodynamic Landau theory can then be epitomized[4] in a series of exact conditions (A)–(D) on the high-symmetry group $\mathfrak{G}_0$, the compatible subgroups $\mathfrak{G}_1$, the acceptable irreducible representations $\mathfrak{D}^{(\star\mathbf{k})(m)}$ of $\mathfrak{G}_0$, and the space-group reduction coefficients in $\mathfrak{G}_0$:

$\mathfrak{G}_1$ is a subgroup of $\mathfrak{G}_0$; (A)

$([^\star\mathbf{k}m]_{(3)} \mid \Gamma 1+)=0$; (B)

$([^\star\mathbf{k}m]_{[2]} \mid \Gamma v)=0$; (C)

$\mathfrak{D}^{(\star\mathbf{k})(m)}$ of $\mathfrak{G}_0$ subduces $\mathfrak{D}^{(\mathbf{\Gamma})(1+)}$ of $\mathfrak{G}_1$; (D)

also, if an acceptable $\mathfrak{D}^{(\star\mathbf{k})(m)}$ is one-dimensional, or if $\mathfrak{D}^{(\star\mathbf{k})(m)}$ of $\mathfrak{G}_0$ subduces only a multiple of $\mathfrak{D}^{(\mathbf{\Gamma})(1+)}$ of $\mathfrak{G}_1$, then the acceptable $\mathfrak{G}_1$ is normal in $\mathfrak{G}_0$, (D.1)

Now we present a new general result, based on the existence of a chain of subgroups. Thus, let $\mathfrak{D}^{(\star\mathbf{k})(m)}$ of $\mathfrak{G}_0$ subduce $\mathfrak{D}^{(\mathbf{\Gamma})(1+)}$ of $\mathfrak{G}_1$ *once*, and let the same $\mathfrak{D}^{(\star\mathbf{k})(m)}$ of $\mathfrak{G}_0$ subduce $\mathfrak{D}^{(\mathbf{\Gamma})(1+)}$ of $\mathfrak{G}_1'$ *once*, where $\mathfrak{G}_1'$ is a subgroup of $\mathfrak{G}_1$. Then consider the density function of $\mathfrak{G}_1'$, viz. $\rho(\mathfrak{G}_1')$. Since the given irreducible space $\Sigma^{(\star\mathbf{k})(m)}$ by hypothesis contains only *one* invariant vector for $\mathfrak{G}_1$, namely $\rho(\mathfrak{G}_1)$, and since $\mathfrak{G}_1'$ is a subgroup of $\mathfrak{G}_1$, it is clear that the invariant vector $\rho(\mathfrak{G}_1')$ must be identical to $\rho(\mathfrak{G}_1)$. That is, given the density $\rho(\mathfrak{G}_1')$, one finds it invariant also under all elements in $\mathfrak{G}_1$. Hence the density function $\rho(\mathfrak{G}_1')$ actually is invariant under the larger group. Alternatively put, this eliminates the transition $\mathfrak{G}_0\to\mathfrak{G}_1'$. The possibility of the transition $\mathfrak{G}_1\to\mathfrak{G}_1'$ succeeding $\mathfrak{G}_0\to\mathfrak{G}_1$ must be examined separately.

[4] J. L. Birman, Phys. Rev. Letters **17**, 1216 (1966).

To summarize: let $\mathfrak{G}_0\supset\mathfrak{G}_1$ mean that $\mathfrak{G}_1$ is a subgroup of $\mathfrak{G}_0$, and $\downarrow$ mean "subduces." We conclude that

if

$$\mathfrak{G}_0\supset\mathfrak{G}_1\supset\mathfrak{G}_1'$$

and

$$\mathfrak{D}^{(\star\mathbf{k})(m)} \text{ of } \mathfrak{G}_0 \downarrow \mathfrak{D}^{(\mathbf{\Gamma})(1+)} \text{ of } \mathfrak{G}_1 \text{ (once)}$$

and

$$\mathfrak{D}^{(\star\mathbf{k})(m)} \text{ of } \mathfrak{G}_0 \downarrow \mathfrak{D}^{(\mathbf{\Gamma})(1+)} \text{ of } \mathfrak{G}_1' \text{ (once)},$$

then the transition

$$\mathfrak{G}_0\to\mathfrak{G}_1' \text{ is eliminated.} \tag{D.2}$$

Condition (D) will be referred to as the subduction criterion. Conditions (D.1) and (D.2) are related to it, and we found (D.2) to be particularly valuable in reducing the number of potentially compatible subgroups.

To (A)–(D), we add the rule[4]

$$\mathfrak{D}^{(\star\mathbf{k})(m)} \text{ of } \mathfrak{G}_0 \text{ corresponds to a physical tensor field.} \tag{E}$$

For a displacive phase transition, a complete set of variables with which to describe the shifts in atom positions within the unit cell are the normal modes. Another general manner by which some subgroups have been eliminated is by recognizing that the assumed shift from their positions in perovskite, as given by the amplitude pattern of a normal mode, leaves the atoms in such positions of high symmetry that added symmetry elements are necessarily present. In this way we recognized that the lower-symmetry group actually must be augmented and so becomes some group of higher symmetry, which is also a compatible subgroup of $\mathfrak{G}_0$. This will be illustrated below.

Observe that (A), (B), (C), (D), (D.1), and (D.2) are exact, within the thermodynamic Landau theory. They may be considered as simultaneous restrictions on the acceptable $\mathfrak{D}^{(\star\mathbf{k})(m)}$ and on the compatible $\mathfrak{G}_1$, and they serve to eliminate the tedious minimization usually needed in this analysis.[2] Our analysis of perovskite was carried out in the framework of the Landau theory to obtain new results for a case of considerable current theoretical[5] and experimental[6] interest. No critical evaluation of the assumptions of the Landau theory will be given.[7]

2. ANALYSIS AND RESULTS

We are concerned, in the perovskite structure[8] O_h^1-Pm3m, with the possibility of second-order phase transition without change of unit cell; the transition is

[5] P. W. Kwok and P. B. Miller, Phys. Rev. **151**, 387 (1966); R. C. Casella, *ibid.* **154**, 743 (1967).

[6] G. Samara, Phys. Rev. **151**, 378 (1966); A. Frova and P. J. Boddy, *ibid.* **153**, 606 (1967).

[7] V. L. Ginzburg, Fiz. Tverd. Tela **2**, 2031 (1960) [English transl.: Soviet Phys.—Solid State **2**, 1824 (1961)]; L. P. Kadanoff *et al.*, Rev. Mod. Phys. **39**, 395 (1967), and references therein.

[8] J. G. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., Inc., New York, 1965), Vol. 2, Appendix A3-4.

TABLE I. The 32 subgroups of O_h^1 with the same unit cell, and the irreducible representations of O_h which subduce the identity representation on each subgroup.[a]

Representations of O_h subducing $\mathfrak{D}^{(\Gamma)(1+)}$	Point group		Space group	
A_{1g}, A_{1u}	O	432	O^1	$P432$
A_{1g}, A_{2g}	T_h	$m3$	T_h^1	$Pm3$
A_{1g}, F_{2g}	D_{3d}	$\bar{3}m$	D_{3d}^5	$R\bar{3}m$
A_{1g}, A_{2u}, F_{2g}, F_{1u}	C_{3v}	$3m$	C_{3v}^5	$R3m$
A_{1g}, A_{2g}, A_{1u}, A_{2u}, F_{1g}, F_{2g}, F_{1u}, F_{2u}	C_3	3	C_3^4	$R3$
A_{1g}, E_g, F_{1g}	C_{4h}	$4/m$	C_{4h}^1	$P4/m$
A_{1g}, A_{1u}, E_g, E_u	D_4	422	D_4^1	$P422$
A_{1g}, A_{2u}, E_g, E_u, F_{2u}	D_{2d}	$\bar{4}2m$	D_{2d}^1	$P\bar{4}2m$
A_{1g}, A_{2u}, E_g, E_u, F_{2u}	D_{2d}	$\bar{4}2m$	D_{2d}^5	$C\bar{4}2m$
A_{1g}, A_{2u}, E_g, E_u, F_{1g}, F_{2u}	S_4	$\bar{4}$	S_4^1	$P\bar{4}$
A_{1g}, A_{2g}, E_g, F_{2g}	D_{2h}	mmm	D_{2h}^1	$Pmmm$
A_{1g}, A_{2g}, E_g, F_{2g}	D_{2h}	mmm	D_{2h}^{19}	$Cmmm$
A_{1g}, A_{2g}, A_{1u}, A_{2u}, E_g, E_u, F_{2g}, F_{2u}	D_2	222	D_2^1	$P222$
A_{1g}, A_{2g}, A_{1u}, A_{2u}, E_g, E_u, F_{2g}, F_{2u}	D_2	222	D_2^6	$C222$
A_{1g}, A_{2g}, A_{2u}, E_g, E_u, F_{2g}, F_{1u}, F_{2u}	C_{2v}	$mm2$	C_{2v}^1	$Pmm2$
A_{1g}, A_{2g}, A_{2u}, E_g, E_u, F_{2g}, F_{1u}, F_{2u}	C_{2v}	$mm2$	C_{2v}^{11}	$Cmm2$
A_{1g}, A_{2g}, A_{2u}, E_g, E_u, F_{2g}, F_{1u}, F_{2u}	C_{2v}	$mm2$	C_{2v}^{14}	$Amm2$
A_{1g}, A_{2g}, E_g, F_{1g}, F_{2g}	C_{2h}	$2/m$	C_{2h}^1	$P2/m$
A_{1g}, A_{2g}, E_g, F_{1g}, F_{2g}	C_{2h}	$2/m$	C_{2h}^3	$C2/m$
A_{1g}, A_{2g}, E_g, F_{1g}, F_{2g}, A_{1u}, A_{2u}, E_u, F_{1u}, F_{2u}	C_2	2	C_2^1	$P2$
A_{1g}, A_{2g}, E_g, F_{1g}, F_{2g}, A_{1u}, A_{2u}, E_u, F_{1u}, F_{2u}	C_2	2	C_2^3	$C2$
A_{1g}, A_{2g}, E_g, F_{1g}, F_{2g}, A_{2u}, E_u, F_{1u}, F_{2u}	C_s	m	C_s^1	Pm
A_{1g}, A_{2g}, E_g, F_{1g}, F_{2g}, A_{2u}, E_u, F_{1u}, F_{2u}	C_s	m	C_s^3	Cm
A_{1g}, A_{2g}, E_g, F_{1g}, F_{2g}	C_i	$\bar{1}$	C_i^1	$P\bar{1}$
A_{1g}, A_{2u}	T_d	$\bar{4}3m$	T_d^1	$P\bar{4}3m$
A_{1g}, A_{2g}, A_{1u}, A_{2u}	T	23	T^1	$P23$
A_{1g}, A_{2g}, A_{1u}, A_{2u}, F_{2g}, F_{2u}	D_3	32	D_3^7	$R32$
A_{1g}, A_{2g}, F_{1g}, F_{2g}	C_{3i}	$\bar{3}$	C_{3i}^2	$R\bar{3}$
A_{1g}, E_g	D_{4h}	$4/mmm$	D_{4h}^1	$P4/mmm$
A_{1g}, A_{1u}, E_g, E_u, F_{1g}, F_{1u}	C_4	4	C_4^1	$P4$
A_{1g}, E_g, F_{1u}	C_{4v}	$4mm$	C_{4v}^1	$P4mm$
A_{1g}, A_{2g}, E_g, F_{1g}, F_{2g}, A_{1u}, A_{2u}, E_u, F_{1u}, F_{2u}	C_1	1	C_1^1	$P1$

[a] Reference 11.

of the displacive type.[9] Since the unit cell does not change, we may, as in another recent analysis,[4] restrict consideration to the irreducible representation of O_h^1 with star Γ [$\mathbf{k}=(0, 0, 0)$], i.e., to the irreducible representations of the point group O_h. The space group O_h^1 has 32 subgroups with the same unit cell.[10] In Table I we list the subgroups of O_h^1 with the same unit cell, and the irreducible representations subducing the identity representation on each subgroup.[11]

Of the 10 irreducible representations of O_h, the representations A_{1g}, E_g, and F_{2g} are unacceptable[4] since they do not satisfy (B). As the physical tensor field which plays a decisive role in the displacive transition, it is natural to choose the optic-branch normal modes at Γ, in perovskite.[12] The symmetry species are[12]

$$\text{optic modes:}\quad 3F_{1u}\oplus F_{2u}. \tag{7}$$

Since Table I shows that many potentially compatible subgroups can only be achieved by use of unacceptable representations (e.g., the space group O^1, etc.) we may eliminate all but 18 such subgroups. In this manner Table II is obtained.

To continue the analysis,[13] we examine each of the remaining subgroups in Table II to ascertain whether the occupiable sites in that subgroup are consistent with the assumptions that they represent atoms slightly displaced from their initial positions in O_h^1. In other words, we are attempting to determine some of the

TABLE II. Those subgroups of O_h^1 with the same unit cell upon which a normal-mode species subduces the identity representation, and the corresponding species.

Normal-mode species subducing $\mathfrak{D}^{(\Gamma)(1+)}$	Space group	
F_{1u}	C_{3v}^5	$R3m$
F_{1u}, F_{2u}	C_3^4	$R3$
F_{2u}	D_{2d}^1	$P\bar{4}3m$
F_{2u}	D_{2d}^5	$C\bar{4}3m$
F_{2u}	S_4^1	$P\bar{4}$
F_{2u}	D_2^1	$P222$
F_{2u}	D_2^6	$C222$
F_{1u}, F_{2u}	C_{2v}^1	Pmm
F_{1u}, F_{2u}	C_{2v}^{11}	Cmm
F_{1u}, F_{2u}	C_{2v}^{14}	Amm
F_{1u}, F_{2u}	C_2^1	$P2$
F_{1u}, F_{2u}	C_2^3	$C2$
F_{1u}, F_{2u}	C_s^1	Pm
F_{1u}, F_{2u}	C_s^3	Cm
F_{2u}	D_3^7	$R32$
F_{1u}	C_4^1	$P4$
F_{1u}	C_{4v}^1	$P4mm$
F_{1u}, F_{2u}	C_1^1	$P1$

[9] W. Kanzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 1; F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Inc., New York, 1962).

[10] *International Tables for X-Ray Crystallography*, edited by N. F. M. Henry and K. Lonsdale (Kynoch Press, Birmingham, England, 1952), Vol. 1.

[11] Notation used is that of E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Co., Inc., New York, 1955).

[12] B. D. Silverman and G. F. Koster, Z. Physik **165**, 334 (1961); V. Dvorak, Phys. Status Solidi **3**, 2235 (1965); also reviewed in Ref. 3.

[13] Additional details are contained in: Senior Honors Thesis in Physics, submitted by Fredric E. Goldrich to University College of Arts and Science, New York University, April 1967 (unpublished).

"free parameters" of the subgroup by our knowledge that a small displacement, consistent with the same unit cell, has occurred. In this fashion the groups C_2^1–$P2$; C_{2v}^1–$Pmm2$; C_4^1–$P4$; C_{2v}^{11}–$Cmm2$; C_2^3–$C2$; D_2^6–$C222$; D_{2d}^1–$P\bar{4}2m$; and D_2^1–$P222$ can be eliminated.

The cases of D_2^6; D_{2d}^1; and D_2^1 are instructive. We see, by inspecting the tables,[10] that the only allowed sites are, in fact, the sites originally occupied in O_h^1. There are thus two possibilities. Either the symmetry of the system is truly tetragonal ($c/a \neq 1$), or it is actually cubic. If the system possesses tetragonal symmetry, but the coordinates of the positions of the atoms with respect to the crystal axes do not change, then the symmetry change corresponds to a deformation of the unit cell without atomic displacement, or, in other words, a strain. The strain tensor, however, transforms according to irreducible representations which were eliminated by earlier criteria, so that a strain may not take part in the transition.

If the symmetry after the transition is cubic, and the atoms have not moved, then there is no transition, because there is no symmetry change—both states are identical. Therefore, the space groups D_{2d}^1, D_2^1, and D_2^6 have been eliminated. We will say in the future that D_{2d}^1, D_2^6, and D_2^1 are "included in O_h^1."

In a similar fashion, it is found that the occupiable sites in C_4^1 actually correspond to C_{4v}^1; that is, given available atoms in $BaTiO_3$, a slight displacement to C_4^1 actually produces the higher symmetry C_{4v}^1. This is a case of a lower-symmetry group included in a higher-symmetry group, and twelve possible displacement patterns have been ruled out through similar arguments. One of these is C_{2v}^{11}, which Haas[14] incorrectly identified as the orthorhombic phase of $BaTiO_3$. In fact, not only is it impossible to achieve C_{2v}^{11} from O_h^1 by means of a second-order phase transition, but the experimental identification of the space group[9] is C_{2v}^{14}.

The final step in the analysis is to verify that indeed each of the remaining eight space groups can be obtained by small displacements which transform as a row of a single acceptable irreducible representation. Using the relevant projection operator for the third row of each of F_{1u} and F_{2u}, this was done. The result is given in Table III, which summarizes our work. Table IV gives the atomic displacements from O_h^1 to each of the compatible subspace groups.

TABLE III. The eight subgroups of O_h^1 with the same unit cell allowed by the subduction criterion, and the corresponding irreducible representations.

Crystal system	Space group		Irreducible representations
Triclinic	C_1^1	$P1$	F_{1u} or F_{2u}
Monoclinic	C_s^1	Pm	F_{1u} or F_{2u}
	C_s^3	Cm	F_{1u}
Orthorhombic	C_{2v}^{14}	$Amm2$	F_{1u} or F_{2u}
Tetragonal	C_{4v}^1	$P4mm$	F_{1u}
	D_{2d}^5	$C\bar{4}2m$	F_{2u}
Trigonal	D_3^7	$R32$	F_{2u}
	C_{3v}^5	$R3m$	F_{1u}

3. DISCUSSION

Of the eight space groups presented in Table III, two have been given by Haas (C_{3v}^5 and C_{4v}^1). The remainder are new. Only those space groups which can be achieved by mode F_{1u} can correspond to a ferroelectric lower-symmetry phase.[15] It follows that a ferroelectric second-order phase transition without cell change can be achieved from the high-symmetry perovskite O_h^1 structure to each of those space groups identified by F_{1u}.

The space groups which may be achieved by mode F_{2u} do not correspond to the occurrence of ferroelectric polarization. In the cubic system the normal-mode representation F_{2u} corresponds to the transformation of components of a second-rank pseudotensor, such as would be constructed from the cross components of macroscopic electric and magnetic fields, E_iH_j. Thus a transition to space group D_{2d}^5; D_3^7; C_{2v}^{14}; C_3^1 or C_1^1 may be accompanied by the appearance of a macroscopic crystal physical property of the symmetry of a second-rank pseudotensor.

It appears that the results given in Table III are as far as one can go if one confines oneself rigorously to the symmetry theory contained in the Landau theory. To go further requires the construction and minimization of the thermodynamic potential G, in order to narrow down still further the possible predictions. For such minimization to be meaningful, one should possess sufficient microscopic information to be able to obtain the exact form of the coefficients in the expansion (4) and so to decide among alternative compatible subgroups. No such completely rigorous theory has yet been advanced, or at any rate none is known to us. In the absence of the complete analysis, it has been proposed[16] that among the compatible subgroups one should choose certain "maximal" ones. This criterion does not seem to be justifiable from a fundamental point of view, but it may possibly be a useful way of selecting more likely candidates in the absence of a rigorous theory. It may be, however, that some physically implausible transitions [e.g., $O_h^1 \rightarrow C_1^1$ which (Table III) according to our result may occur as second order] can only be eliminated depending upon quantitative calculations, based on the full theory.

We conclude by emphasizing the importance of obtaining experimental information on the full space-

[14] C. Haas, Phys. Rev. **140**, A863 (1965).

[15] A. F. Devonshire, Advan. Phys. **3**, 85 (1965); W. Cochran, *ibid.* **9**, 387 (1960).

[16] E. Ascher, Phys. Letters **20**, 352 (1966); and private communication (to be published).

TABLE IV. Atomic displacements for symmetry-lowered $BaTiO_3$.

Irreducible representation	Allowed space group		Displacement from higher-symmetry position Ba	Ti	O_3
F_{1u}	C_1^1	$P1$	(x, y, z)	(x', y', z')	(x'', y'', z'') (x''', y''', z'') (x''', y'', z''')
F_{2u}	C_1^1	$P1$	$(0, 0, 0)$	$(0, 0, 0)$	$(0, \bar{y}, z)$ $(x, 0, \bar{z})$ $(\bar{x}, y, 0)$
F_{1u}	C_s^1	Pm	$(x, y, 0)$	$(x', y', 0)$	$(x'', y'', 0)$ $(x''', y''', 0)$ $(x''', y'', 0)$
F_{2u}	C_s^1	Pm	$(0, 0, 0)$	$(0, 0, 0)$	$(0, \bar{y}, 0)$ $(\bar{x}, 0, 0)$ $(x, y, 0)$
F_{1u}	C_s^3	Cm	(x, x, z)	(x', x', z')	(x'', y, z'') (y, x'', z'') (y, y, z''')
F_{1u}	C_{2v}^{14}	$Amm2$	$(0, y, y)$	$(0, y', y')$	$(0, y'', y'')$ $(0, z, y'')$ $(0, y'', z)$
F_{2u}	C_{2v}^{14}	$Amm2$	$(0, 0, 0)$	$(0, 0, 0)$	$(0, y, y)$ $(0, 0, \bar{y})$ $(0, \bar{y}, 0)$
F_{1u}	C_{4v}^1	$P4mm$	$(0, 0, z)$	$(0, 0, z')$	$(0, 0, z'')$ $(0, 0, z'')$ $(0, 0, z''')$
F_{2u}	D_{2d}^5	$C\bar{4}2m$	$(0, 0, 0)$	$(0, 0, 0)$	$(0, 0, z)$ $(0, 0, \bar{z})$ $(0, 0, 0)$
F_{2u}	D_3^7	$R32$	$(0, 0, 0)$	$(0, 0, 0)$	$(0, y, \bar{y})$ $(\bar{y}, 0, y)$ $(y, \bar{y}, 0)$
F_{1u}	C_{3v}^5	$R3m$	(x, x, x)	(x', x', x')	(z, x'', x'') (x'', z, x'') (x'', x'', z)

group symmetry (not merely the "crystal class") of lower symmetry phases which have arisen by second-order transitions. Very few such determinations are available, against which the predictions of theory can be checked. Some exceptions are: the tetragonal phase of $BaTiO_3$, identified[17] experimentally as C_{4v}^1, and the orthorhombic phase of $BaTiO_3$, identified[17] as C_{2v}^{14}. However, in $BaTiO_3$ the transition $O_h^1 \rightarrow C_{4v}^1$ is first order. In the binary system $K(NbTa)O_3$, a second-order transition has been identified[18] as a tetragonal phase, but the space group of the latter is merely surmised[18] to be that of the analogous tetragonal perovskite. This illustrates and emphasizes the need for precise structural information.

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