

## Phase Transitions in Ferroelectric and Antiferroelectric Crystals

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Group theory is applied to phase transitions in ferroelectric and antiferroelectric crystals. The procedure is given to derive for a paraelectric crystal with a given space group all possible ferroelectric states which can exist for arbitrarily small values of the polarization. A knowledge of the space groups of the crystal above and below the transition point makes it possible to predict whether a second-order phase transition is possible. The predictions made for a number of ferroelectric and antiferroelectric crystals are in agreement with available experimental data. The classification of ferroelectric phase transitions given by Aizu and Devonshire's theory for  $\text{BaTiO}_3$  follow quite naturally from these symmetry considerations. In an appendix the symmetry properties of second-order phase transitions leading to structures which cannot be described by a three-dimensional space group (e.g., magnetic spirals) are discussed.

### INTRODUCTION

**F**ERROELECTRIC properties have been observed in a large number of solids.<sup>1-3</sup> The transition from the paraelectric state to the ferroelectric state is accompanied by small atomic displacements producing electrical-dipole moments in the crystal. As a consequence there is an anomalous behavior of the dielectric constant near the transition point. The symmetry of the ferroelectric state is lower than the symmetry of the paraelectric state.

In some crystals a transition from a paraelectric to an antiferroelectric state has been observed.<sup>1,2</sup> In these cases also shifts of atoms occur, producing electrical-dipole moments in the crystal. Here, however, these dipole moments compensate each other in such a way that the unit cell of the antiferroelectric state has no resultant dipole moment.

The nature of phase transitions in these crystals has been studied extensively. Devonshire<sup>4,5</sup> has given a phenomenological theory which describes the change of the electrical polarization with temperature, and the effect of an electrical field or a mechanical stress on the polarization. The possible types of symmetry occurring in ferroelectric crystals were studied by Aizu.<sup>6,7</sup>

Both first- and second-order phase transitions are observed. A first-order phase transition is an abrupt change from one phase to another, accompanied by a discontinuous change of the lattice parameters. At the transition point latent heat is liberated. If the transition is from a paraelectric to a ferroelectric state, the polarization changes abruptly at the transition temperature. A second-order phase transition is a more gradual change of the crystal without latent heat; the lattice parameters and the polarization are continuous, al-

though the temperature derivatives may change abruptly at the transition point.

Megaw<sup>2</sup> has related the nature of the phase transitions to the symmetry of the crystal, but she does not give the necessary and sufficient conditions for second-order phase transitions. These conditions can be obtained in a rigorous form from Landau's theory of phase transitions.<sup>8,9</sup> It is remarkable that this theory, published as early as 1937, has been applied only to a few actual phase transitions in metal alloys.<sup>9-11</sup> Recently, Landau's considerations were used to describe phase transitions in magnetic crystals,<sup>12</sup> in weakly ferromagnetic crystals,<sup>13,14</sup> and in crystals with the spinel structure.<sup>15</sup>

### LANDAU'S THEORY OF PHASE TRANSITIONS

In general one can distinguish the following types of change of a crystal:

(a) A continuous change without a change of symmetry. In this case there is no phase transition.<sup>16</sup>

(b) An abrupt change by a first-order phase transition. At the transition temperature there are two phases in equilibrium with each other. Such a first-order phase transition is possible between any two phases, the only condition being that the free energies of the two phases become equal at the transition temperature. There are no symmetry requirements for a first-order phase transition to be possible.

(c) In a second-order phase transition the properties of the crystal change gradually until at a certain transi-

<sup>8</sup> L. D. Landau, *Physik Z. Sowjetunion* **11**, 26 (1937).

<sup>9</sup> L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press Ltd., London, 1962), Chap. 14.

<sup>10</sup> E. M. Lifshitz, *J. Phys. (U.S.S.R.)* **6**, 61 (1942).

<sup>11</sup> E. M. Lifshitz, *J. Phys. (U.S.S.R.)* **6**, 251 (1942).

<sup>12</sup> J. O. Dimmock, *Phys. Rev.* **130**, 1337 (1963).

<sup>13</sup> I. Dzyaloshinski, *J. Phys. Chem. Solids* **4**, 241 (1958).

<sup>14</sup> E. A. Turov, *Zh. Eksperim. i Teor. Fiz.* **42**, 1582 (1962) [English transl.: *Soviet Phys.—JETP* **15**, 1098 (1962)].

<sup>15</sup> C. Haas, *J. Phys. Chem. Solids* **26**, 1225 (1965).

<sup>16</sup> There exists one special type of second-order phase transitions in which there is no change of symmetry. These transitions are related to condensation phenomena, and are described in terms of an essentially positive internal parameter. Examples are the transition between the normal and the superconducting state, and the  $\lambda$  transition in liquid helium.

<sup>1</sup> W. Känzig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 1.

<sup>2</sup> H. D. Megaw, *Ferroelectricity in Crystals* (Mehuen & Co., Ltd., London, 1957).

<sup>3</sup> F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press Ltd., London, 1962).

<sup>4</sup> A. F. Devonshire, *Phil. Mag.* **40**, 1040 (1949).

<sup>5</sup> A. F. Devonshire, *Phil. Mag.* **42**, 1065 (1951).

<sup>6</sup> K. Aizu, *Phys. Rev.* **133**, A1350 (1964).

<sup>7</sup> K. Aizu, *Phys. Rev.* **136**, A753 (1964).

tion temperature the change is complete. At each temperature, even at the transition point, only one phase exists so that a second-order phase transition is a transition within one phase and not between two phases as was the case for a first-order phase transition. This type of transition is only possible if certain stringent conditions for the symmetry above and below the transition point are fulfilled.

In order to derive these symmetry conditions,<sup>9</sup> consider some function  $\rho_0(\mathbf{r})$ , for example, the density function for electrons or for a particular type of atom in the crystal, which represents the full symmetry of the crystal.  $\rho_0(\mathbf{r})$  will be invariant under all operations of the space group of the crystal. If the crystal changes slightly and continuously in such a way that the symmetry of the crystal is lowered, the new density function  $\rho(\mathbf{r})$  can be written as

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \Delta\rho(\mathbf{r}), \quad (1)$$

where  $\Delta\rho(\mathbf{r})$  is the small change due to the lowering of symmetry. The symmetry group of  $\rho(\mathbf{r})$  cannot contain symmetry operations not contained in the symmetry group of  $\rho_0(\mathbf{r})$ , and consequently the group of  $\rho(\mathbf{r})$  is a subgroup of the group of  $\rho_0(\mathbf{r})$ . Therefore a condition for a second-order phase transition is that there must be a change of symmetry in such a way that the symmetry group of one state of the crystal is a subgroup of that of the other state (condition I).

It is well known from group theory<sup>17,18</sup> that an arbitrary function can always be written as a sum of functions transforming as the irreducible representations of a symmetry group. Therefore, it is possible to write

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \sum_n \sum_i c_{ni} \phi_{ni}(\mathbf{r}). \quad (2)$$

The functions  $\phi_{ni}(\mathbf{r})$  form a basis for the  $n$ th irreducible representation of the symmetry group which leaves  $\rho_0(\mathbf{r})$  invariant. The number of functions  $i$  for a particular representation  $n$  is equal to the dimension of the representation. Because a function transforming as the identical representation gives rise to no change of symmetry, the identical representation will be omitted from the summation over  $n$ .

It can be only by accident if two independent types of change (i.e., changes corresponding to different irreducible representations  $n$ ) would set in at exactly the same temperature. In general, if two independent changes occur, then there will be two phase transitions. Therefore, a second-order phase transition involves a change of the crystal corresponding to a single irreducible representation (condition II).

Consequently, one can omit the summation over  $n$ , and investigate

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \sum_i c_i \phi_i(\mathbf{r}) \quad (3)$$

<sup>17</sup> H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons Inc., London, 1949).

<sup>18</sup> J. S. Lomont, *Applications of Finite Groups* (Academic Press Inc., New York, 1964).

for a change of the crystal corresponding to a particular irreducible representation.

The change of the crystal corresponds, of course, to a change of the free energy. For small values of the coefficients  $c_i$  one can write the free energy  $G$  as a power series in  $c_i$ . Substituting  $c_i = \eta\gamma_i$  with  $\sum_i \gamma_i^2 = 1$ , one obtains

$$G = G_0 + a\eta f^{(1)} + A\eta^2 f^{(2)} + B\eta^3 f^{(3)} + C\eta^4 f^{(4)} + \dots \quad (4)$$

The coefficients  $a, A, B, C$ , etc., are functions of the temperature and  $f^{(l)}$  is a homogeneous function of order  $l$  in the coefficients  $\gamma_i$ .

The operations of the group of  $\rho_0$  will transform the coefficients  $\gamma_i$  into each other. The free energy does not change by these operations. Therefore in the free energy only functions  $f^{(l)}$  occur which are invariant under all operations of the group of  $\rho_0$ . Because first-order invariants exist only for the identical representation which is not considered, the linear term in Eq. (4) vanishes. Furthermore, only one quadratic-invariant exists for any representation.

$$G = G_0 + A\eta^2 + B\eta^3 f^{(3)} + C\eta^4 f^{(4)} + \dots \quad (5)$$

The actual stable state of the crystal is found by minimizing  $G$  with respect to  $\eta$  and  $\gamma_i$ . From the conditions for stability  $\partial G/\partial\eta = 0$  and  $\partial^2 G/\partial\eta^2 > 0$ , one finds that the state  $\eta = 0$  is stable for  $A > 0$ , whereas for  $A < 0$  the stable state must have  $\eta \neq 0$ . Therefore, a phase transition from the state of high symmetry  $\eta = 0$  to a state with a lower symmetry could occur at the point where  $A = 0$ . However, for the crystal to be stable at the point where  $A = 0$  and  $\eta = 0$ ,  $G$  must increase both for small positive and negative changes of  $\eta$ . This can not be the case if  $Bf^{(3)} \neq 0$ . Therefore a second-order phase transition is possible only if third-order terms in the free energy are zero, i.e., the function  $f^{(3)}$  should vanish by symmetry (condition III).<sup>19</sup>

Conditions I, II, and III are the necessary and sufficient symmetry conditions for a second-order phase transition to be possible. For the special case that one space group is a subgroup of the other with half the number of symmetry operations, one can easily show that all three conditions are fulfilled.

Even if conditions I, II, and III are fulfilled, the transition will occur as a first-order phase transition if  $C < 0$ .<sup>9</sup>

The symmetry of crystals is given by the space group, the group of translations, rotations, and reflections which leave the crystal invariant. The irreducible representations are characterized by vectors  $\mathbf{k}$  in the reciprocal lattice, representing the properties for translations.<sup>20</sup> If  $\phi_{\mathbf{k}}(\mathbf{r})$  is one of the basis functions of a representation, characterized by  $\mathbf{k}$ , then a translation  $\mathbf{t}$

<sup>19</sup> If  $f^{(3)}$  does not vanish by symmetry, one can have a second-order phase transition only if both  $A$  and  $B$  vanish at the same time. Such a situation can occur only at isolated points in a two-dimensional phase diagram (Ref. 9). These cases will not be considered in this paper.

<sup>20</sup> G. F. Koster, *Space Groups and Their Representations* (Academic Press Inc., New York, 1964).

which leaves the lattice-invariant transforms  $\phi_{\mathbf{k}}(\mathbf{r})$  into  $e^{i\mathbf{k}\cdot\mathbf{r}}\phi_{\mathbf{k}}(\mathbf{r})$ .

Landau<sup>9</sup> derived a fourth condition for a second-order phase transition on basis of the requirement for stability of the crystal against spatial inhomogeneity. According to this analysis, a second-order phase transition corresponding to a representation characterized by  $\mathbf{k}$  is only possible if  $-\mathbf{k}=\mathbf{k}+\mathbf{g}$  ( $\mathbf{g}$  is zero, or a vector of the reciprocal lattice of the state of high symmetry), or if  $\mathbf{k}$  is a vector for which the proper symmetry group (i.e., the group of rotations and reflections that leave  $\mathbf{k}$  invariant or change  $\mathbf{k}$  into  $\mathbf{k}+\mathbf{g}$ ) contains symmetry planes and axes intersecting in a point (condition IV).

The validity of this condition has been questioned by Dimmock,<sup>12</sup> both on theoretical grounds and on the basis of experimental evidence for phase transitions in some rare-earth metals. In these metals, second-order phase transitions have been observed between a paramagnetic state and a spiral or sinusoidal spin configuration with a periodicity which is not a simple multiple of the crystallographic lattice parameters.<sup>21</sup> These second-order phase transitions do not obey condition IV.

In our opinion (see Appendix) condition IV properly distinguishes between two types of second-order phase transitions. Only for transitions obeying condition IV, the state of the crystal with the lower symmetry has a three-dimensional periodic structure, described by one of the space groups. If condition IV is not obeyed, a second-order phase transition is still possible, but then the three-dimensional periodicity is lost in the state of lower symmetry, and the symmetry of this state cannot be described by one of the three-dimensional space groups. Structures of the latter type have been observed in magnetic crystals as mentioned,<sup>21</sup> and probably also in order-disorder transitions in alloys,<sup>22,23</sup> but not yet in ferroelectric crystals.

### DISCUSSION OF THEORIES FOR FERROELECTRIC CRYSTALS

Some remarks will be made regarding the relation between Landau's theory of phase transitions and theories for ferroelectric crystals:

(a) Aizu<sup>24</sup> distinguishes three types of phase transitions in ferroelectric crystals: "primitive," "complex," and others.

For "primitive" phase transitions, the symmetry group of the paraelectric state contains the symmetry elements of the ferroelectric state plus the so-called  $F$  operation which makes the polarization change sign. In this case the space group of the ferroelectric state will be a subgroup of the space group of the paraelectric state with half the number of symmetry elements. Conse-

quently, for these "primitive" phase transitions, a second-order phase transition is always possible.

For "complex" phase transitions, the symmetry group of the paraelectric state contains the group of the ferroelectric state, the  $F$  operation and one or more independent extra symmetry operations. The symmetry group of one state is in this case a subgroup of the symmetry group of the other state but not with half the number of symmetry elements. Condition I is fulfilled, but in order to decide whether a particular "complex" transition is possible as a second order phase transition the other two conditions should be investigated.

For transitions which are neither "complex" nor "primitive," one space group is not a subgroup of the other. Therefore such transitions do not fulfill condition I, and can occur only as first order phase transitions.

(b) For phase transitions from a paraelectric to a ferroelectric state the parameters  $\eta$  and  $\gamma_i$  are directly related to the electrical polarization  $\mathbf{P}$ . This correspondence will be used to illustrate the relation with Devonshire's theory for BaTiO<sub>3</sub>.<sup>4,5</sup>

BaTiO<sub>3</sub> has in the high-temperature paraelectric state the cubic perovskite structure, space group  $O_h^1-Pm3m$ . Consider a change of the crystal by small atomic displacements such that a ferroelectric state is obtained. Because an electrical polarization vector transforms as the representation  $T_{1^-}$ , with  $\mathbf{k}=(000)$ , of the factor group  $O_h^{17}$ , the change to a ferroelectric state will certainly correspond to this representation.

In order to obtain the functions  $f^{(l)}$  occurring in the expression for the free energy, it is necessary to find the independent invariants of order  $l$  in the coefficients  $\gamma_i$ . The number of independent invariants of order  $l$  is equal to the number of times the identical representation  $A_{1^+}$  occurs in the symmetrical direct product  $T_{1^-}$  of order  $l$ . Using the techniques of group theory<sup>17,18</sup> one finds that for  $l=2, 4,$  and  $6$  there are 1, 2, and 3 independent invariants. Products with  $l$  odd of a representation which is antisymmetric with respect to inversion (such as  $T_{1^-}$ ) cannot contain the identical representation. The general form of the functions  $f^{(l)}$  is found to be

$$\begin{aligned} f^{(2)} &= 1; & f^{(4)} &= 1 + \lambda(\gamma_1^4 + \gamma_2^4 + \gamma_3^4); \\ f^{(6)} &= 1 + \mu(\gamma_1^6 + \gamma_2^6 + \gamma_3^6) + \xi\gamma_1^2\gamma_2^2\gamma_3^2, \end{aligned} \quad (6)$$

where  $\lambda, \mu,$  and  $\xi$  are parameters which depend on the temperature.

In order to find the actual stable state of the crystal the free energy should be minimized with respect to the coefficients  $\gamma_i$ . Considering only terms of the lowest order in  $\eta$  one obtains the equations

$$\frac{\partial f^{(4)}}{\partial \gamma_i} - 2g\gamma_i = 0 \quad \text{or} \quad 4\lambda\gamma_i^3 - 2g\gamma_i = 0, \quad (7)$$

where  $g$  is a Lagrange multiplier taking into account that  $\gamma_1^2 + \gamma_2^2 + \gamma_3^2 = 1$ . These Eqs. (7) have the solutions

$$\begin{aligned} (\alpha) \quad & \gamma_1 = 1, \quad \gamma_2 = 0, \quad \gamma_3 = 0, \\ (\beta) \quad & \gamma_1 = 1/\sqrt{2}, \quad \gamma_2 = 1/\sqrt{2}, \quad \gamma_3 = 0, \\ (\gamma) \quad & \gamma_1 = 1/\sqrt{3}, \quad \gamma_2 = 1/\sqrt{3}, \quad \gamma_3 = 1/\sqrt{3}. \end{aligned}$$

<sup>21</sup> R. J. Elliott, Phys. Rev. **124**, 346 (1961).

<sup>22</sup> L. Guttman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 174.

<sup>23</sup> R. Sato and R. S. Roth, Phys. Rev. **124**, 1833 (1961).

<sup>24</sup> K. Aizu, J. Phys. Soc. Japan **19**, 918 (1964).

The states corresponding to these solutions ( $\alpha$ ), ( $\beta$ ), and ( $\gamma$ ) are the only ferroelectric states of the crystal which can be stable for arbitrarily small deviations from the cubic state.

The quantities  $\gamma_1$ ,  $\gamma_2$ , and  $\gamma_3$  transform in precisely the same way as the components  $P_x$ ,  $P_y$ , and  $P_z$  of the polarization, and therefore one can substitute  $P_x$ ,  $P_y$ , and  $P_z$  for  $\eta\gamma_1$ ,  $\eta\gamma_2$ , and  $\eta\gamma_3$

$$G = G_0 + A(P_x^2 + P_y^2 + P_z^2) + C\{(P_x^2 + P_y^2 + P_z^2)^2 + \lambda(P_x^4 + P_y^4 + P_z^4)\} + F\{(P_x^2 + P_y^2 + P_z^2)^3 + \mu(P_x^6 + P_y^6 + P_z^6) + \xi P_x^2 P_y^2 P_z^2\} + \dots \quad (8)$$

Devonshire used this equation (with  $\xi=0$ ) to describe the properties of  $\text{BaTiO}_3$ . The three solutions ( $\alpha$ ), ( $\beta$ ), and ( $\gamma$ ) represent in fact the three ferroelectric phases of  $\text{BaTiO}_3$ , with, respectively, the polarization  $\mathbf{P}$  parallel to the (100) axes [solution ( $\alpha$ ), tetragonal], parallel to (110) [solution ( $\beta$ ), orthorhombic], and parallel to (111) [solution ( $\gamma$ ), rhombohedral].

The treatment given above illustrates how symmetry arguments can be used to derive the equation for the free energy and to determine the possible ferroelectric states of a crystal with a given symmetry in the paraelectric state.

(c) Aizu<sup>25</sup> has pointed out that in ferroelectric crystals with a low symmetry there can be some ambiguity as to how to define the polarization; in fact in ferroelectric crystals one is not interested in the total electrical dipole moment per unit cell, but only in the part which can be switched by an electric field. The parameter  $\eta$  emerging from the derivation given above represents in fact precisely this part of the polarization.

#### APPLICATION TO PHASE TRANSITIONS IN SOME FERROELECTRIC AND ANTI-FERROELECTRIC CRYSTALS

The theory will be used to decide in which cases a second-order phase transition is possible.

(a) Barium titanate ( $\text{BaTiO}_3$ ) and a number of other compounds have in the high-temperature paraelectric state the cubic perovskite structure, with space group  $O_h^1 - Pm\bar{3}m$ .<sup>1,3</sup> At lower temperatures  $\text{BaTiO}_3$  shows a succession of phase transitions: the cubic phase (c) transforms at 120°C into a tetragonal ferroelectric phase  $\alpha$ . This phase  $\alpha$  transforms at 5°C into an orthorhombic phase  $\beta$ , which at -90°C transforms into a rhombohedral phase  $\gamma$ . The phases  $\alpha$ ,  $\beta$ , and  $\gamma$  are ferroelectric; the space groups are, respectively,  $C_{4v}^1 - P4mm$ ,  $C_{2v}^{11} - Cmm$ , and  $C_{3v}^5 - R\bar{3}m$ . Because the unit cell does not change (except for small deformations) the reciprocal lattice vector  $\mathbf{k}$  for all possible transitions between the phases  $c$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  is  $\mathbf{k}=(000)$ , a vector satisfying condition IV.

First transitions from the paraelectric state  $c$  to any of the ferroelectric states  $\alpha$ ,  $\beta$ ,  $\gamma$  will be discussed. The space groups of  $\alpha$ ,  $\beta$ , and  $\gamma$  are subgroups of the space group of  $c$ , and correspond to a single irreducible representation. It was shown already that no third-order invariants exist. Therefore the conditions for second-order phase transitions are fulfilled, and a transition from the cubic state  $c$  to any of the ferroelectric states  $\alpha$ ,  $\beta$ , and  $\gamma$  is possible as a second-order phase transition.

The discussion of transitions between the ferroelectric states is particularly simple because the space groups of  $\alpha$ ,  $\beta$ , and  $\gamma$  are not subgroups of one another. This is because each of these space groups contains a symmetry operation not contained in the other two space groups. Therefore transitions between the ferroelectric phases  $\alpha$ ,  $\beta$ , and  $\gamma$  can never occur as second-order phase transitions, and consequently will always be first-order phase transitions.

In  $\text{BaTiO}_3$ , and also in  $\text{KNbO}_3$  which undergoes the same sequence of phase transitions, all observed transitions  $c \rightarrow \alpha$ ,  $\alpha \rightarrow \beta$ , and  $\beta \rightarrow \gamma$  are found to be first-order phase transitions, as indicated by appreciable discontinuous changes of the lattice parameters at the transition points.<sup>1,3</sup> An interesting confirmation of the prediction that the transition  $c \rightarrow \alpha$  is possible as a second-order transition is shown in the binary system  $\text{KNb}_{1-x}\text{Ta}_x\text{O}_3$ , which for  $x < 0.8$  undergoes the same sequence of phase transitions as  $\text{BaTiO}_3$ .<sup>26</sup> It was found that the transition  $c \rightarrow \alpha$  is a first order one for  $x < 0.55$ , but changes to a second-order transition for  $x > 0.55$ . According to our consideration such a change would be impossible, and in fact was not found, for the transitions  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$ .

(b) Lead zirconate ( $\text{PbZrO}_3$ ) has in the high-temperature paraelectric state also the cubic perovskite structure, but undergoes at 230°C a first-order phase transition to an antiferroelectric state with space group  $C_{2v}^8 - Pba2$ .<sup>1,3</sup> By symmetry arguments it will be shown that a transition of this type must necessarily be a first-order phase transition.

The antiferroelectric state of  $\text{PbZrO}_3$  has an orthorhombic unit cell which has 8 times the volume of the cubic unit cell of the perovskite structure. The primitive lattice parameters of the orthorhombic cell can be written as  $\mathbf{a}=(110)$ ,  $\mathbf{b}=(\bar{2}20)$  and  $\mathbf{c}=(002)$ , if (100), (010), and (001) are the primitive vectors of the (slightly distorted) cubic cell. The reciprocal lattice can be found in the usual way from the relations  $\mathbf{k}_a = V^{-1}(\mathbf{b} \times \mathbf{c})$ ,  $\mathbf{k}_b = V^{-1}(\mathbf{c} \times \mathbf{a})$ ,  $\mathbf{k}_c = V^{-1}(\mathbf{a} \times \mathbf{b})$ , where  $V = \mathbf{a}(\mathbf{b} \times \mathbf{c})$  is the volume of the unit cell. One finds  $\mathbf{k}_a = (\frac{1}{2} \frac{1}{2} 0)$ ,  $\mathbf{k}_b = (-\frac{1}{4} \frac{1}{4} 0)$  and  $\mathbf{k}_c = (00\frac{1}{2})$ .

The irreducible representations of the space group which may correspond to these vectors are representations with  $\mathbf{k}_1 = (00\frac{1}{2})$ ,  $\mathbf{k}_2 = (\frac{1}{2} \frac{1}{2} 0)$ ,  $\mathbf{k}_3 = (\frac{1}{2} \frac{1}{2} \frac{1}{2})$ ,  $\mathbf{k}_4 = (-\frac{1}{4} \frac{1}{4} 0)$ , and  $\mathbf{k}_5 = (-\frac{1}{4} \frac{1}{4} \frac{1}{2})$ . It is clear that if the

<sup>25</sup> K. Aizu, Rev. Mod. Phys. 34, 550 (1962).

<sup>26</sup> S. Triebwasser, Phys. Rev. 114, 63 (1959).

properties of the antiferroelectric state were described, for example, by functions of the representation  $\mathbf{k}_1$  only, the translational symmetry would be higher than observed because these functions are invariant for translations (100) and the antiferroelectric state is not. The only functions of the representation with  $\mathbf{k}_5 = (-\frac{1}{4} \frac{1}{4} \frac{1}{2})$  which are invariant for all translations of the antiferroelectric state are functions transforming as  $e^{\pm i\mathbf{k}_5 \cdot \mathbf{r}}$ . However, these functions are invariant also for a translation (112), which is not a translation of the antiferroelectric state. Therefore, if the antiferroelectric state could be described by these functions only, its symmetry would be higher than observed. In this way it is possible to show that the observed antiferroelectric state of  $\text{PbZrO}_3$  can be described only by a linear combination of functions corresponding to at least two irreducible representations. Consequently, the transition from the perovskite structure to the antiferroelectric structure of  $\text{PbZrO}_3$  does not fulfill condition II, and will be possible only as a first-order phase transition.

(c) In a large group of ferroelectrics the transition from the paraelectric to the ferroelectric state is "primitive."<sup>7</sup> Consequently, a second-order phase transition is possible in all these compounds. In most cases experimentally a second-order phase transition is observed. Examples are the phase transitions in triglycine sulfate, Rochelle salt, potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ), and antimony sulfoiodide ( $\text{SbSI}$ ).<sup>1-3</sup>

(d) Ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) has a transition from a paraelectric tetragonal structure (space group  $D_{2d}^{12} - I42d$ , with four molecules per unit cell) to an antiferroelectric structure (space group  $D_2^4 - P2_12_12_1$ , four molecules per unit cell) at  $148^\circ\text{K}$ .<sup>1,3</sup>

The space group  $D_2^4$  is a subgroup of  $D_{2d}^{12}$ . For the paraelectric structure the reciprocal lattice is generated by the vectors  $\mathbf{k}_a = (011)$ ,  $\mathbf{k}_b = (101)$ , and  $\mathbf{k}_c = (110)$ , the reciprocal lattice of the antiferroelectric structure is generated by  $\mathbf{k}'_a = (100)$ ,  $\mathbf{k}'_b = (010)$ , and  $\mathbf{k}'_c = (001)$ . Therefore the transition corresponds to a representation with  $\mathbf{k} = (100)$ . Because  $-\mathbf{k} = \mathbf{k} + (200)$ , and  $(200)$  is a vector  $\mathbf{g}$  of the reciprocal lattice of the paraelectric state,  $\mathbf{k}$  fulfills condition IV.

Third-order terms will transform as the third-order direct product of the representation with  $\mathbf{k} = (100)$ . Third-order invariants can exist only if this product contains the identical representation. However, it is not possible to construct a sum of three vectors out of the vectors (100), (010), and (001) equal to a vector  $\mathbf{g}$  of the reciprocal lattice of the paraelectric state. Consequently, third order invariants cannot exist, and because the other conditions are also fulfilled, a second-order phase transition is possible.

Experimentally the nature of the transition is not very clear. Probably, the transition is a first-order one, because the crystal is reported to crumple if it passes the transition.<sup>1,3</sup>

(e) Ammonium bisulfate ( $\text{NH}_4\text{HSO}_4$ ) occurs in three structures: state I with space group  $C_{2h}^5 - P2_1/c$  is

stable above  $-3^\circ\text{C}$ , state II with space group  $C_s^2 - Pc$  is stable between  $-3^\circ\text{C}$  and  $-119^\circ\text{C}$ , and state III with space group  $C_1^1 - P1$  is stable below  $-119^\circ\text{C}$ ;<sup>3</sup> only state II is ferroelectric. The monoclinic unit cell in all three structures contains 8 molecules, and the vector  $\mathbf{k}$  for all transitions will be (000). The group  $C_1^1$  is a subgroup of  $C_s^2$  with half the number of symmetry elements,  $C_s^2$  is a subgroup of  $C_{2h}^5$  with half the number of symmetry elements. Consequently, the phase transitions  $\text{I} \rightarrow \text{II}$  at  $-3^\circ\text{C}$  and  $\text{II} \rightarrow \text{III}$  at  $-119^\circ\text{C}$  are possible as second-order phase transitions.

Experimentally the transition  $\text{I} \rightarrow \text{II}$  is reported to be a second-order transition, the  $\text{II} \rightarrow \text{III}$  transition a first-order one.<sup>1,3</sup>

(f) Methylammonium aluminum sulfate dodecahydrate,  $(\text{NH}_3\text{CH}_3) \text{Al} (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , belongs to space group  $C_2^2 - P2_1$  in the ferroelectric state, and to space group  $T^4 - P2_13$  in the paraelectric state.<sup>3</sup> The vector of the transition is  $\mathbf{k} = (000)$  because the unit cell is the same for both states of the crystal. Space group  $C_2^2 - P2_1$  is a subgroup of space group  $T^4 - P2_13$ . However, because the number of symmetry elements is not doubled, the transition is not primitive but complex, and third-order invariants should be investigated.

The electrical-polarization vector transforms as the three-dimensional representation  $T$ , and therefore the transition corresponds to this representation. The symmetrical direct product  $(T \times T \times T)_{\text{sym}}$  is found to be  $A + 3T$ . Because this product contains the identical representation  $A$ , there will be a third-order term in the free energy (this third-order term can be written as  $BP_xP_yP_z$ ). Consequently, the transition from the paraelectric state is not possible as a second-order transition. Experimentally, a first-order phase transition is observed.<sup>3</sup>

## CONCLUSION

In conclusion, the information which can be obtained by applying Landau's theory to ferroelectrics and antiferroelectrics will be summarized. First, it is possible to find the most general expansion of the free energy in terms of the polarization by making use only of the space group of the paraelectric state. Second, it is possible to find for a given symmetry of the paraelectric state all ferroelectric states which can exist for arbitrarily small values of the polarization. Second-order phase transitions from the paraelectric state are only possible to these ferroelectric states. Third, for crystals where a second-order phase transition is observed, the possible space groups of the ferroelectric state can be easily enumerated if the space group of the paraelectric state is known. Finally, if the space groups of the two states of the crystal are known, then in some cases it is possible to predict with certainty that the phase transition must be a first order transition. The experimental data discussed are in agreement with these predictions.

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### APPENDIX: TWO TYPES OF SECOND-ORDER PHASE TRANSITIONS

In this Appendix the validity of condition IV will be discussed. The discussion will be based on a derivation which differs from that given by Landau.<sup>9</sup>

The representation of space groups<sup>20</sup> are characterized by "stars"  $\{\mathbf{k}\}$ ; such a star is a set of  $\mathbf{k}$  vectors invariant for all rotations and reflections of the space group. The basis functions belonging to an irreducible representation characterized by  $\{\mathbf{k}\}$  are  $\phi_{\mathbf{k}i}$ , where  $\mathbf{k}$  are vectors from  $\{\mathbf{k}\}$ .

Consider in the density function  $\rho(\mathbf{r})$  of a crystal contributions of representations  $\{\mathbf{k}\}$  with slightly different values of  $\{\mathbf{k}\}$ :

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) + \sum_{\{\mathbf{k}\}} \sum_{\mathbf{k} \text{ in } \{\mathbf{k}\}} \sum_i \eta_{\{\mathbf{k}\}} \gamma_{\mathbf{k},i} \phi_{\mathbf{k}i}. \quad (\text{A1})$$

The free energy of the crystal is given by

$$G = G_0 + \sum_{\{\mathbf{k}\}} A_{\{\mathbf{k}\}} \eta_{\{\mathbf{k}\}}^2 + \dots \quad (\text{A2})$$

For stars  $\{\mathbf{k}\}$  differing only slightly from each other, the corresponding basis functions are related to each other by

$$\phi_{\mathbf{k}+\delta\mathbf{k},i}(\mathbf{r}) = \phi_{\mathbf{k}i}(\mathbf{r}) e^{i\delta\mathbf{k}\mathbf{r}}. \quad (\text{A3})$$

The function  $A_{\{\mathbf{k}\}}$  will change continuously for variations in  $\{\mathbf{k}\}$ . Because all stars  $\{\mathbf{k}\}$  are invariant for rotations and reflections of the space group,  $A_{\{\mathbf{k}\}}$  will exhibit in  $\mathbf{k}$  space the full symmetry for rotations and reflections.

Suppose that there is a second-order phase transition with a change of the crystal corresponding to a particular irreducible representation  $\{\mathbf{k}_1\}$ . The condition for stability of the crystal in the region of high symmetry is that  $A_{\{\mathbf{k}\}} > 0$  for all representations  $\{\mathbf{k}\}$ . The condition for the occurrence of a second-order phase transition corresponding to a representation  $\{\mathbf{k}_1\}$  is that at the transition point,  $A_{\{\mathbf{k}_1\}} = 0$ , and  $A_{\{\mathbf{k}\}} > 0$  for all other representations. Therefore, a condition for a second-order phase transition corresponding to a representation  $\{\mathbf{k}_1\}$  is that  $A_{\{\mathbf{k}\}}$  is a minimum at  $\{\mathbf{k}_1\}$ .

$A_{\{\mathbf{k}\}}$  can be written as a power series in the neighborhood of  $\{\mathbf{k}_1\}$ :

$$A_{\{\mathbf{k}_1+\delta\mathbf{k}\}} = A_{\{\mathbf{k}_1\}} + \alpha_{\{\mathbf{k}_1\}} \delta\mathbf{k} + \dots \quad (\text{A4})$$

$A_{\{\mathbf{k}\}}$  has a minimum at  $\{\mathbf{k}_1\}$  only if the vector  $\alpha_{\{\mathbf{k}_1\}}$  vanishes at the transition point. This is possible in two ways.

### Second-Order Phase Transitions of Type I

Consider the case that  $\alpha_{\{\mathbf{k}_1\}}$  vanishes by symmetry.  $A_{\{\mathbf{k}_1+\delta\mathbf{k}\}}$  is invariant for all operations of the group,  $\mathbf{k}_1$  is invariant for all operations of the proper symmetry group of  $\mathbf{k}_1$ . As a consequence,  $\alpha_{\{\mathbf{k}_1\}}$  must be invariant also for all operations of the proper symmetry group  $\mathbf{k}_1$ . Therefore,  $\alpha_{\{\mathbf{k}_1\}}$  vanishes by symmetry only if the proper symmetry group of  $\mathbf{k}_1$  has no invariant vectors. This is the case if  $-\mathbf{k}_1 = \mathbf{k}_1 + \mathbf{g}$ , or if the proper symmetry group of  $\mathbf{k}_1$  contains symmetry axes and planes intersecting in a point. Thus, the condition that  $\alpha_{\{\mathbf{k}_1\}}$  vanishes by symmetry leads directly to condition IV. This is not surprising because the consideration of spatial variations of the coefficients in Landau's analysis is in fact equivalent to the consideration of a set of representations with slightly different values of  $\{\mathbf{k}\}$ .

Dimmock<sup>12</sup> has criticized Landau's derivation using the argument that the introduction of a spatial variation of the coefficients is not allowed because the density function has been developed already in a complete set of functions. However, we obtained condition IV without the use of a spatial variation of the coefficients.

For phase transitions obeying condition IV, only very special values of  $\mathbf{k}_1$  are allowed. It is easily seen that these  $\mathbf{k}_1$  values can always be written as simple fractions of a small reciprocal lattice vector  $\mathbf{g}$ . Consequently, the symmetry of the crystal below the transition point can be described by an ordinary three-dimensional space group, with a unit cell which is a simple multiple of the original unit cell.

### Second-Order Phase Transitions of Type II

Even if  $\alpha_{\{\mathbf{k}\}}$  does not vanish by symmetry, it is possible that this quantity vanishes at the transition point, and that a second-order phase transition occurs. However, in such a case the value of  $\mathbf{k}_1$  will not be a special point in reciprocal space. A consequence of this is that the symmetry of the crystal in the state of lower symmetry cannot be described by a three-dimensional space group. In at least one direction the lattice periodicity is entirely lost, due to a component in the density function proportional to  $e^{i\mathbf{k}_1\mathbf{r}}$ , with a period  $2\pi/|\mathbf{k}_1|$  which has no simple relation with the crystallographic periodicity of the crystal above the transition temperature.

Below the transition point in general the period of the extra contribution to the density function will change continuously with temperature. This is possible without any phase transition, because it involves no change of symmetry (in fact, translation symmetry is lost already at the transition point).

The characteristics of such second-order phase transitions of type II, corresponding to a representation not obeying condition IV, represent correctly the experimentally observed behavior of the transitions in magnetic crystals with spiral spin configuration.