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Ferroelectricity and Antiferroelectricity of a Crystal Containing Rotatable Polar Molecules*

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We have investigated the dielectric properties of a CsCl type crystal made up by insertion of ions into the body center sites of a simple cubic array of rotatable polar molecules. Owing to the Lorentz field exerted by the dipoles themselves, a non-uniform distribution in orientation of the polar molecules is predicted below a certain critical temperature. The main results obtained are as follows: (1) It is shown that the crystal is antiferroelectric so long as the polarizability of the central ions is small, half of the dipoles being partially oriented parallel to and the other half antiparallel to one of the cube edges. On the other hand, if the polarizability of the ions is larger than a certain threshold value, the crystal is ferroelectric, all the dipoles being partially oriented parallel to each other. (2) The dielectric constant-temperature curves calculated for antiferroelectric cases show a variety of forms according to the polarizabilities of both components. For some specimens they are almost flat throughout the region around their own critical temperatures, while for other specimens they can show such sharp peaks that they are hardly discernible from those of ferroelectric crystals, which always show very sharp peaks tending to infinity. (3) Below their respective critical temperatures, the dielectric constant should decrease with increasing dc bias in a ferroelectric crystal, while in an antiferroelectric crystal it should increase slightly under the same condition. (4) If a sufficiently strong field is applied to an antiferroelectric crystal at just below its critical temperature, it will be forced to make a momentary transition to a ferroelectric one, the change being accompanied by an abrupt increase of polarization.

It is suggested that most of the phenomenological predictions derived with this model may, qualitatively at least, be valid also for other models which have ions capable of displacement instead of freely rotatable dipoles, as is really the case with the well-known $BaTiO_3$ and the like.

I. INTRODUCTION

ANOMALOUS peaks are frequently observed in the dielectric constant-temperature curves of crystals containing or composed of rotatable polar molecules, and are generally known as the phase changes arising from hindered molecular rotation.[1] Considering the form of the lambda-points of the peaks, the transitions must represent some kind of cooperational phenomenon, and the hindering potential acting upon any molecule on the lattice must in any case depend upon the state of rotation of the molecules themselves.

Several attempts have been made to construct an explicit form for the torque potential. For example, Kirkwood[2] has formulated a theory based upon a short-range interaction of the form $(\epsilon/2)\cos\gamma$ for a pair of neighboring molecules, the axes of which are inclined at an angle γ to each other. If the hindering potential in the crystal concerned really arises from short-range forces, such as steric hindrance or the like, which can be effective only between the molecules in contact, his treatment will yield a good approximation. On the contrary, however, if it is certain that most of the hindering torque arises from the dipole-dipole interaction, as it does in the case with which we are going to deal, the nearest-neighbor treatment may be inadequate, as Kirkwood himself mentioned in his article. This is, in the first place, because the dipole forces are long range in nature and, what is still more important, because their peculiar directional nature invalidates the expression in terms of a single parameter γ. For example, two dipoles parallel to each other have a negative energy if they are on the same line, whereas they can have even a positive energy if they are arranged side by side.

The present paper aims to show how a fairly satisfactory theory can be formulated if we replace Kirkwood's potential by the Lorentz field. For the sake of simplicity, we shall start with a simple cubic array of rotatable dipoles, for we know well what is the most suitable set of sublattices into which a simple cubic lattice can be decomposed.[3] Besides, we shall insert ions into the body center sites of the array in order to clarify an important role played by the polarizabilities of the crystal components. It will be shown how interesting characteristics unknown in magnetic substances are theoretically expected for dielectric crystals only.

Very recently Kittel[4] has developed a theory of antiferroelectricity. The present theory will add to it from another point of view, though the model treated here is perhaps too simplified to be realized in nature.

II. DISTRIBUTION FUNCTIONS

To start with, let us consider a simple cubic array of dipoles without the ions at the body center sites. Electrostatic energy eigenvalues of such an array have been fully discussed by Luttinger and Tisza.[3] They have shown that in the state of lowest energy which the system should assume at 0°K, half of the dipoles, namely those on the lattice denoted by 1 in Fig. 1, orient themselves parallel to, say, the $+z$ direction while the other half, on the lattice denoted by 2, orient themselves parallel to the $-z$ direction.

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[1] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, London, 1936), second edition, p. 810.

[2] J. G. Kirkwood, J. Chem. Phys. **8**, 205 (1940).

[3] J. M. Luttinger and L. Tisza, Phys. Rev. **70**, 954 (1946).

[4] C. Kittel, Phys. Rev. **82**, 729 (1951).

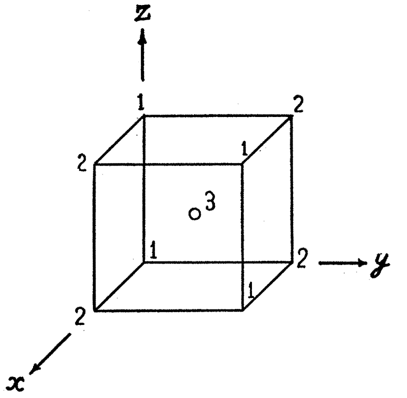

FIG. 1. Classification of sublattices. The sites 1 and 2 are occupied by polar molecules; the site 3 by ions.

For such an ordered configuration, full use of symmetry considerations may be made in calculating the inner field. It turns out that the field acting on lattice 1 is really pointing in the $+z$ direction while that on the lattice 2 points in the $-z$ direction.

As the temperature is raised, however, this ordered configuration will be gradually disturbed by thermal agitation, and a rigorous calculation of the inner field becomes very difficult. That is, although we are sure that the inner field will then decay in some kind of cooperative manner, yet a rigorous evaluation of it seems almost impracticable because one must carry out a summation over a great many electrostatic forces, each arising from an individual dipole oriented at random.

Viewed from another angle, however, this very process of summation seems at the same time to have the advantage of smoothing out most of the microscopic fluctuations in the local field from site to site. So we may assume without much harm that the inner field F_i acting on a lattice i is homogeneous throughout the specified lattice, though of course it can be different from the inner field F_j acting on another lattice j; its value, to this approximation, may be calculated by supposing that every molecule had just the average moment taken over the specified lattice to which it belongs. That is, we shall assume that the field is to be determined if we only know the macroscopic polarizations P_i of the sublattices.[5,6]

Now we shall add the ions into the body center sites and designate them by the number 3. On account of our assumption

$$F_i=E+\sum_{j=1}^{3} f_{ij}P_j/\epsilon_0;\quad i=1,2,3, \tag{1}$$

where f_{ij} are the Lorentz factors, the values of which may be obtained from a paper by McKeehan;[7]

$$\begin{gathered} f_{ij}=f_{ji},\\ f_{11}=f_{22}=\tfrac{1}{3}+0.4260,\\ f_{12}=\tfrac{1}{3}-0.4260,\\ f_{13}=f_{23}=f_{33}=\tfrac{1}{3}. \end{gathered} \tag{2}$$

The polarizations P_i are in their turn to be determined by the local field. The field acts to concentrate the distribution of dipoles around itself as closely as possible, in opposition to disruptive influences due to thermal agitation. If $n_i(\omega)$ gives the probability for any one molecule on lattice i to be in an orientation ω, then the part of the polarization due to the permanent molecular moment, μ, is given by

$$P_{di}=(\mu/2v)\int \cos\theta\, n_i(\omega)d\omega,\quad i=1,2, \tag{3}$$

where v is the volume of a unit cell, and θ the angle between z-axis and the orientation ω.

The most probable form of $n_i(\omega)$ under a given external field E and a given temperature T is of course to be determined from the minimum condition for the free energy of the crystal.

The entropy S associated with a macroscopic state specified by a set of distribution functions $n_i(\omega)$ is clearly

$$S=-k\sum_{i=1}^{2}\int n_i(\omega)\log n_i(\omega)d\omega, \tag{4}$$

k being the Boltzmann constant.

The internal energy U is given by definition

$$U=-\sum_{i=1}^{3}\int F_i dP_i=-E\sum_{i=1}^{3}P_i-\frac{1}{2\epsilon_0}\sum_{i=1}^{3}\sum_{j=1}^{3}f_{ij}P_iP_j. \tag{5}$$

The polarizations are each composed of two terms, since every molecule has, besides the orientation polarization, also the electronic polarization as well as the ionic polarization induced by the local field. Namely,

$$P_i=P_{di}+P_{\alpha i},\quad i=1,2;\quad P_3=P_{\alpha 3}, \tag{6}$$

together with

$$P_{\alpha i}=\epsilon_0\alpha_1F_i/2v,\ i=1,2;\quad P_{\alpha 3}=\epsilon_0\alpha_3F_3/v, \tag{7}$$

where α_1 and α_3 are the polarizabilities of the molecules and ions respectively, excluding those due to the permanent dipoles.

Substituting (6) and (7) into (1), we can eliminate all the $P_{\alpha i}$ terms and can express the polarizations P_i in terms of only $n_i(\omega)$ and E. Then Eq. (5) can be transformed into the form

$$U=-\epsilon_0\kappa E^2-hE\sum_{i=1}^{2}P_{di}-\frac{1}{2\epsilon_0}\sum_{i=1}^{2}\sum_{j=1}^{2}g_{ij}P_{di}P_{dj}, \tag{8}$$

where κ, h, and g_{ij} are simple but somewhat lengthy expressions involving α_i and f_{ij}. Their explicit forms,

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

[6] S. Roberts, Phys. Rev. **81**, 865 (1951).

[7] L. W. McKeehan, Phys. Rev. **43**, 913 (1933).

however, will be omitted here, since only certain combinations of them are of importance, and if combined they become rather simple as seen later.

Following the procedure in Kirkwood's theory,[2] extremalization of the free energy F, i.e.,

$$F=U-TS, \tag{9}$$

by means of the calculus of variations, with respect to the functions $n_i(\omega)$, subject to the normalization restraint,

$$\int n_i(\omega)d\omega=1, \quad i=1, 2, \tag{10}$$

leads to the following set of the most probable distribution functions:

$$n_i(\omega)=\frac{x_i}{4\pi \sinh x_i}\exp(x_i \cos\theta), \quad i=1, 2. \tag{11}$$

The parameters x_i must satisfy the following simultaneous equations

$$\frac{x_i}{\sigma}=\frac{2v}{\mu}h-\epsilon_0 E+\sum_{j=1}^{2} g_{ij}L(x_j), \quad i=1, 2, \tag{12}$$

where $\sigma=\mu^2/\epsilon_0 2vkT$, and $L(x)$ is the Langevin function,

$$L(x)=\coth x-1/x=(x/3)-(x^3/45)+(2x^5/945)-\cdots(x\ll 1). \tag{13}$$

Substituting (11) into (3), we obtain as dipolar parts

$$P_{di}=(\mu/2v)L(x_i), \quad i=1, 2. \tag{14}$$

The total polarizations of respective sublattices can easily be written in terms of these Langevin functions (see the next section).

Our approximation is clearly just equivalent to that of the Weiss molecular field theory of ferromagnetism, but seems to fit the present problem more closely, because the dipole forces underlying the dielectric phenomena are essentially long range in nature.

III. ANTIFERROELECTRICITY AND FERROELECTRICITY

When $E=0$, Eqs. (12) are reduced to

$$\frac{x_i}{\sigma}=\sum_{j=1}^{2} g_{ij}L(x_j), \quad i=1, 2. \tag{15}$$

If nonzero roots of x_i, of minimum free energy, are obtainable from these simultaneous equations, then the sublattices would be spontaneously polarized. From the symmetry of the equations, it is easy to see that either $x_1=x_2$ or $x_1=-x_2$. These two solutions correspond respectively to ferroelectric and antiferroelectric states, for which the dipolar polarizations are respectively oriented parallel and antiparallel to each other.[8]

(i) Antiferroelectricity

Putting $x_1=x=-x_2$, Eqs. (15) are reduced to

$$x/\sigma=(g_{11}-g_{12})L(x). \tag{16}$$

As is well known in the Weiss theory of ferromagnetism, there exists a critical value of σ, equal to $3/(g_{11}-g_{12})$, below which Eq. (16) has no real solution different from zero, and above which a single nonzero positive real root x, of minimum free energy, exists. This situation leads to a phase change of the second kind with a transition temperature, T_a, given by

$$T_a=(\mu^2/6k\epsilon_0 v)(g_{11}-g_{12}). \tag{17}$$

Substituting (17) into (16), we get a formula defining x as an implicit function of the reduced temperature T/T_a, namely

$$3L(x)/x=T/T_a. \tag{18}$$

Now it is easy to show that

$$g_{11}-g_{12}=(f_{11}-f_{12})\Big/\left\{1-\frac{\alpha_1}{2v}(f_{11}-f_{12})\right\}^2. \tag{19}$$

The polarizations of the lattices are calculated to be

$$\left.\begin{aligned} P_1&=-P_2=\frac{\mu}{2v}L(x)\Big/\left\{1-\frac{\alpha_1}{2v}(f_{11}-f_{12})\right\} \\ P_3&=0. \end{aligned}\right\} \tag{20}$$

(ii) Ferroelectricity

Putting $x_1=x_2=x$, Eqs. (15) are reduced to

$$x/\sigma=(g_{11}+g_{12})L(x). \tag{21}$$

In a similar manner to that used in (i), we can get a critical temperature

$$T_f=(\mu^2/6k\epsilon_0 v)(g_{11}+g_{12}), \tag{22}$$

and instead of (18) a similar relation

$$3L(x)/x=T/T_f. \tag{23}$$

Now it is easy to show that

$$g_{11}+g_{12}=\frac{2}{3}\Big/\left\{1-\frac{1}{3}\left(\frac{\alpha_1}{v}+\frac{\alpha_3}{v}\right)\right\}^2. \tag{24}$$

The polarizations of the lattices are calculated to be given by

$$\left.\begin{aligned} P_1&=P_2=\frac{1-\frac{1}{3}(\alpha_3/v)}{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)}\frac{\mu}{2v}L(x), \\ P_3&=\frac{\frac{2}{3}(\alpha_3/v)}{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)}\frac{\mu}{2v}L(x). \end{aligned}\right\} \tag{25}$$

(iii) Specific Heat Anomaly

The internal energy U, Eq. (8), can be transformed by means of (14), (17), and (22), if $E=0$, to

$$U=-(3k/2v)T_c L^2(x), \tag{26}$$

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[8] H. Takahashi discussed for the first time the possibilities for both ferroelectric and antiferroelectric dipole arrangements in perovskite type crystals by means of the Lorentz field correction as used by Slater; he presented his theory at the Symposium on Dielectrics, held by the Physical Society of Japan at T.I.T., on April 1, 1950. Published by the Society in hectograph.

where T_c should read either T_a or T_f according to the type of the crystal concerned. Hence we have at once as the specific heat associated with rotational configurations, for one mole of the crystal,

$$\frac{C_v}{R}=\frac{x^2L'(x)}{1-3(T_c/T)L'(x)}, \tag{27}$$

R being the gas constant. Equation (27) is just the same as the one Kirkwood obtained; it yields at the transition point a lambda-type peak with a discontinuity of $2.5R$ at the high temperature side. Besides, it tends to a finite value, R, as the temperature approaches 0°K.

Since the relation between C_v and T/T_c is common for both ferroelectric and antiferroelectric cases, it is quite impossible to discriminate between them by means of only caloric measurements.

(iv) Relative Stability of the Two Solutions

It is easy to write the free energy (9) in the following explicit form:

$$F=\frac{kT}{2v}\sum_{i=1}^{2}\left[\log\frac{x_i}{4\pi\sinh x_i}+\frac{x_i}{2}L(x_i)-\frac{h\mu E}{2kT}L(x_i)\right]. \tag{28}$$

When $E=0$, the last term drops out; the remaining quantity in the bracket decreases monotonically with increasing $1/T$, because the derivative $\partial(F/T)/\partial(1/T)=U$ is always negative as seen from (26). Also, x increases monotonically with increasing $1/T$ as seen from Eq. (18) or Eq. (23).

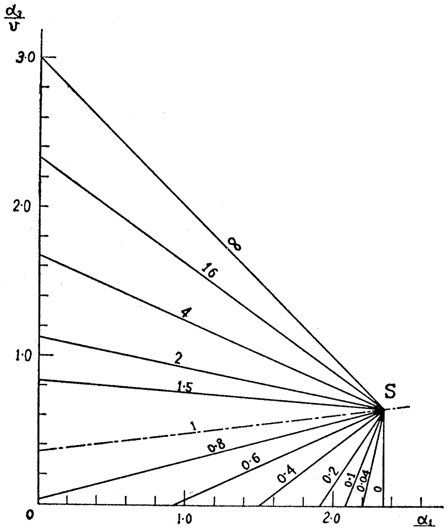

FIG. 2. The iso-Q lines: $Q=T_f/T_a$. All straight lines go through a singular point with the co-ordinates ($\alpha_1/v=2.3474$, $\alpha_3/v=0.6526$). In the region above the line $Q=1$, which is drawn as a chain line, the ferroelectric phase is more stable; in the region below it the antiferroelectric phase is more stable.

Suppose an arbitrary temperature T is given. Then a greater x, and accordingly a smaller free energy would be obtained if a case is chosen wherein the given temperature corresponds to a lower reduced temperature. That is to say, between ferroelectric and antiferroelectric cases, the one that has a higher critical temperature should be more stable.

By means of (17), (19), (22), and (24), the ratio Q of the two critical temperatures can be expressed in terms of the polarizabilities and the Lorentz factors;

$$Q=\frac{T_f}{T_a}=\frac{\frac{2}{3}}{\{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)\}^2}\bigg/\frac{(f_{11}-f_{12})}{\{1-(\alpha_1/2v)(f_{11}-f_{12})\}^2} \tag{29}$$

If an arbitrary value is given to Q, Eq. (29) defines a straight line in an $\alpha_1/v-\alpha_3/v$ plane, several of these lines are shown in Fig. 2. In the region below the special line for which $Q=1$, or

$$\alpha_3/v=0.3462+0.1304(\alpha_1/v), \tag{30}$$

the sublattices should be polarized in an antiferroelectric manner, while in the region above it they should be polarized in a ferroelectric manner. All lines go through a singular point S with the coordinates ($\alpha_1/v=2.3474$, $\alpha_3/v=0.6526$).

IV. DIELECTRIC CONSTANT

The electric displacement, D, namely

$$D=\epsilon_0E+\sum_{i=1}^{3}P_i, \tag{31}$$

can be written in terms of E and P_{di} by means of (1), (2), (6), and (7); i.e.,

$$D=\epsilon_0E+\frac{\alpha_1/v+\alpha_3/v}{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)}\epsilon_0E+\frac{1}{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)}\frac{\mu}{2v}\{L(x_1)+L(x_2)\}, \tag{32}$$

where x_i are to be obtained from Eqs. (12). The third term is not a linear function of x_i, and the x_i in their turn are not linear functions of the field strength E. Therefore, the dielectric constant may vary with a biasing dc field; this effect will be discussed in the next section. We shall here investigate only the initial value of the dielectric constant so defined that

$$[dD/d(\epsilon_0E)]_{E=0}=K. \tag{33}$$

The derivative of x_i with respect to E can be calculated from Eqs. (12), where the relations easily proved from direct calculation,

$$h=\tfrac{3}{2}(g_{11}+g_{12}), \tag{34}$$

may be utilized. Thus we get finally

$$K=1+\frac{\alpha_1/v+\alpha_3/v}{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)}+\frac{3}{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)}\,\frac{3(T_f/T)L'(x)}{1-3(T_f/T)L'(x)}, \tag{35}$$

where the value of x is to be obtained as a function of reduced temperature from (18) or (23) according to the type of stable solution. It is especially to be emphasized that the last term always contains T_f whether or not the crystal concerned is really ferroelectric.

$L'(x)/T$ tends to zero as the temperature approaches 0°K, so that the value of K at 0°K, K_0, consists of only first two terms;

$$K_0=1+\frac{\alpha_1/v+\alpha_3/v}{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)}, \tag{36}$$

or, if solved inversely with respect to the polarizabilities, we get the famous Clausius-Mosotti equation that

$$\frac{\alpha_1}{v}+\frac{\alpha_3}{v}=3\frac{K_0-1}{K_0+2}. \tag{37}$$

Substituting this into (35), we obtain

$$K=K_0+(K_0+2)\frac{3(T_f/T)L'(x)}{1-3(T_f/T)L'(x)}. \tag{38}$$

In a ferroelectric case, x is a function of T_f/T only, so that K is dependent only upon the reduced temperature in addition to K_0. Of course we are supposing that, even if there exist ferroelectric domains, the domain boundaries cannot move under such weak fields as are used in ordinary methods for measuring dielectric constants. Otherwise, Eq. (38) will not apply well to the observed values.

As T approaches T_f, $3(T_f/T)L'(x)$ tends to unity, so that the value of K goes to infinity at the transition point.

If $T>T_f$, then $L'(x)$ is always equal to $\frac{1}{3}$, so that we get

$$K=K_0+(K_0+2)T_f/(T-T_f). \tag{39}$$

Comparing this with the well-known Curie-Weiss law,

$$K=K_0+C/(T-T_p), \tag{40}$$

we see at once that the Curie constant C is

$$C=(K_0+2)T_f, \tag{41}$$

and that the paraelectric Curie point T_p is

$$T_p=T_f. \tag{42}$$

It turns out that if K_0 happens to be very large, the Curie constant C can be far larger than T_f. This is rather a remarkable result because it has been generally believed that, so far as the phase change concerned really arises from a system of rotatable dipoles, C must necessarily be of the same order of magnitude as T_f itself.[5]

In an antiferroelectric case, x is no longer a function of T_f/T but of T_a/T, so that when T approaches the critical temperature T_a, $3(T_f/T)L'(x)$ tends to not one but to $T_f/T_a=Q$. Consequently, the value of K at the Curie point, K_c, remains finite for this case, namely

$$K_c=K_0+(K_0+2)Q/(1-Q). \tag{43}$$

Or we can express the ratio Q in terms of the two special values on the $K-T$ curve, namely K_0 and K_c;

$$Q(=T_f/T_a)=(K_c-K_0)/(K_c+2). \tag{44}$$

Substituting this into (35), we can get a formula most convenient for practical calculation of the $K-T$ curve of a given antiferroelectric crystal,

$$K=K_0+(K_0+2)\frac{Q3(T_a/T)L'(x)}{1-Q3(T_a/T)L'(x)}. \tag{45}$$

If $T>T_a$, Eq. (45) leads to

$$K=K_0+(K_0+2)QT_a/(T-QT_a). \tag{46}$$

Comparing this with the Curie-Weiss law, we find that

$$C=(K_0+2)QT_a, \tag{47}$$

$$T_p=QT_a(=T_f). \tag{48}$$

From (47) we see that, if K_0 is very large and moreover if $K_c \gg K_0$, namely $Q \doteqdot 1$, C can again be very large compared with the transition temperature T_a. Since Q must be less than unity in order that an antiferroelectric state may be realized, the paraelectric Curie temperature for an antiferroelectric crystal should in general be lower than its transition temperature T_a.

Whereas the K–T curves for ferroelectric crystals are, roughly speaking, always similar to each other notwithstanding an arbitrary choice of the parameter K_0, and so especially if $K_0 \gg 2$, the K–T curves for antiferroelectric crystals can show great variety of form for different choices of the parameters, K_0 and K_c. For examples, two extremely different forms are shown in Fig. 3. It may be seen that the curve (a) in the figure is of a form closely resembling that observed with some kinds of crystals known as containing rotatable polar molecules.

Besides, it is to be emphasized that the magnitude of the permanent electric moment of the molecules, μ, only influences the temperature scale as seen from Eqs. (17) and (22), but does not influence at all the value of dielectric constant itself. This is so entirely because the most important parameters, K_0 and K_c, are both completely determined by the polarizabilities of the crystal components. By means of Eqs. (29), (37), and (44) we can at once calculate the iso-K_0 lines as well as

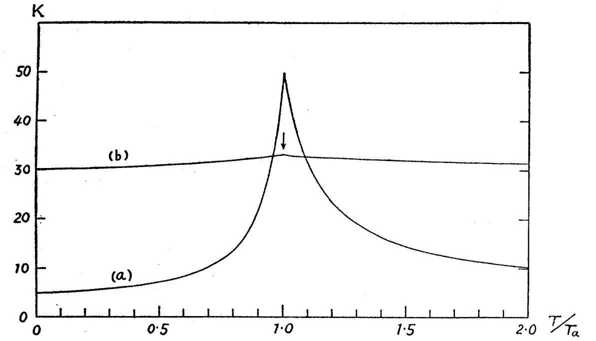

FIG. 3. Two examples of antiferroelectric $K-T$ curves; (a) for a crystal with $K_0=5$ and $K_c=50$; (b) for a crystal with $K_0=30$ and $K_c=33$.

the iso-K_c lines, the results being shown in Fig. 4. In the triangular region, above the line denoted by $K_c=$infinity, for stable ferroelectric solutions, K_c is of course always infinity.

It may also be seen from Fig. 4 that, if both K_0 and K_c of a crystal happens to be very large, a point representative of the crystal should lie very near to the singular point S in the figure. In the neighborhood of S, the crystals may be very sensitive to any change, however slight, in the polarizabilities as well as in the cell volume. By way of illustration, we show in Table I the sets of polarizabilities calculated respectively for three specimens with very different peak values. The points representative of the three crystals described in Table I are thus situated within less than 0.5 percent from each other, so that they may be almost indiscernible if plotted in a figure of as small a size as Fig. 4. The $K-T$ curves of the last two examples are shown in Fig. 5.

It is also seen that, in a certain special case at least, even the $K-T$ curve for an antiferroelectric crystal can attain an extraordinarily high value at its Curie point, though such a sharp peak is indeed unknown in antiferromagnetic cases. Therefore, if, on the other hand, K_c remains finite in a ferroelectric crystal as it actually does in many substances, it may happen that the entire $K-T$ curves resemble each other so much that it may be almost impossible to discriminate between ferroelectrics and antiferroelectrics from their $K-T$ curves alone.

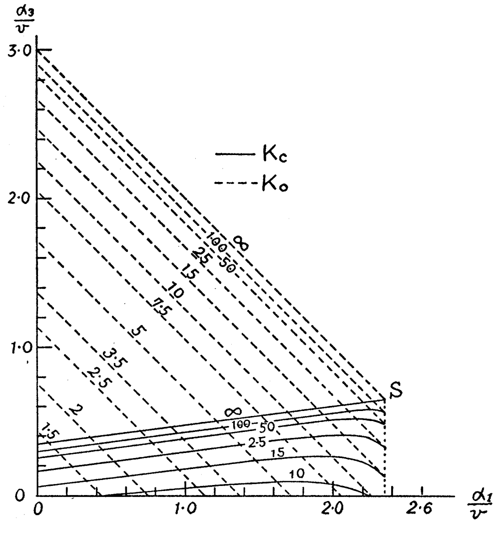

FIG. 4. The dashed lines represent the iso-K_0 lines; the solid lines represent the iso-K_c lines. In the triangular region above the straight line denoted by $K_c=$infinity, i.e., the same line as that shown by a chain line in Fig. 2, K_c is everywhere infinity.

V. RESPONSE TO A DC BIASING FIELD

In order to look for the points of contrast available to discriminate between ferroelectric and antiferroelectric crystals, we shall investigate their response to a dc biasing field. As seen in Sec. IV, the electric displacement (32) contains a nonlinear term composed of the Langevin functions, so that some variation of K should in general be expected under a biasing field.

TABLE I. Polarizabilities calculated for three specimens with different peak values.

Specimens K_0	 K_c	α_1/v	α_3/v
100	1600	2.2719	0.6399
100	3200	2.2707	0.6411
100	infinity[a]	2.2695	0.6423

[a] The value tabulated here is the right lower end, corresponding to $Q=1$, of a line,

$$(\alpha_1/v)+(\alpha_3/v)=2.9118,\quad 0.6423\leq(\alpha_3/v)\leq 2.9118,$$

representing the general solutions for the condition $K_0=100$ and $K_c=$infinity.

By means of the fundamental equations (12) together with (32), we get for an antiferroelectric case, to the second power in E,

$$\left[\sum_{i=1}^{2}\frac{dL(x_i)}{d\epsilon_0E}\right]_E=2\left[L'(x)\frac{dx}{d\epsilon_0E}\right]_0$$
$$+\left[\frac{L'''(x)\{1-3(T_a/T)L'(x)\}+9(T_a/T)\{L''(x)\}^2}{\{1-Q3(T_a/T)L'(x)\}\{1-3(T_a/T)L'(x)\}}\right]_0$$
$$\times\left(\frac{dx}{d\epsilon_0E}\right)_0^3(\epsilon_0E)^2,\quad (49)$$

where the suffixes outside the bracket denote respectively the values under E and zero field. The quantity x in the right-hand side is to be obtained from Eq. (18).

The first term contributes to the initial value of the dielectric constant, while the second term contributes to the change of K under a field E. By means of the series expansion (13) of the Langevin function, it is easy to prove that the second term is indeed positive, so that K should increase with increasing bias, though slowly at first since it is proportional to E^2.

On the other hand, for a ferroelectric case, we obtain

$$\left[\sum_{i=1}^{2}\frac{dL(x_i)}{d\epsilon_0 E}\right]_E=2\left[L'(x)\frac{dx}{d\epsilon_0 E}\right]_0+\left[\frac{2L''(x)}{1-3(T_f/T)L'(x)}\left(\frac{dx}{d\epsilon_0 E}\right)^2\right]_0\epsilon_0 E. \quad (50)$$

As is easily seen, the second term is negative; accordingly K should decrease with increasing bias.

Hence the response to a biasing field, occurring in opposite directions, may be available as a convenient criterion for discerning between the two types of dielectric crystals, though of course these effects might be perceptible only in the immediate vicinity of the Curie point.

If the temperature is above the critical point, the difference between ferroelectric and antiferroelectric dipole configurations disappears. And there K decreases with increasing dc bias, as is seen from Fig. 7 in the next section.

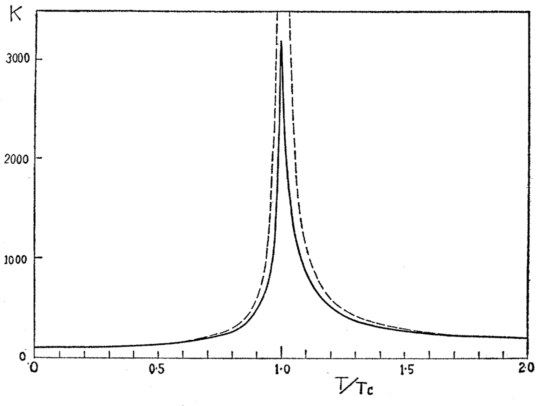

FIG. 5. The antiferroelectric and ferroelectric $K-T$ curves. The solid curve is for an antiferroelectric case with $K_0=100$ and $K_c=3200$; the dashed curve is for a ferroelectric case with $K_0=100$ and $K_c=$infinity. T_c should read either T_a or T_f according to their nature.

VI. *D-E* CURVES AND A FORCED TRANSITION

Though the D-E curves for ferroelectric crystals are very familiar already, those for antiferroelectric crystals have not been discussed yet. We shall therefore take up this problem.

Taking a sum and difference of the fundamental Eqs. (12), we get at once the following set of equations convenient for the present purpose:

$$L(x_1)-\tfrac{1}{3}(T/T_a)x_1=L(x_2)-\tfrac{1}{3}(T/T_a)x_2, \quad (51)$$

$$\tfrac{1}{3}(T/T_f)(x_1+x_2)-\{L(x_1)+L(x_2)\}=(6v/\mu)\epsilon_0 E. \quad (52)$$

From these, we can easily calculate the D-E curves for a given temperature T.

By way of illustration, we shall show the result at a temperature, say, $T=0.9837T_a$. In Fig. 6, the function $L(x)-xT/3T_a$ is shown plotted against x. Equation (51) requires that each set of the roots x_i must always lie on a horizontal line, so that we get a series of the sets of points such as NN', OO', PP', and so forth. If an arbitrary set among these is substituted into Eq. (52), then we can find a field strength E which is necessary to maintain the specified set as stable roots. Besides, from Eq. (14) we can get the value of dipolar polarizations for this set of roots. The results thus calculated are shown plotted in Fig. 7.

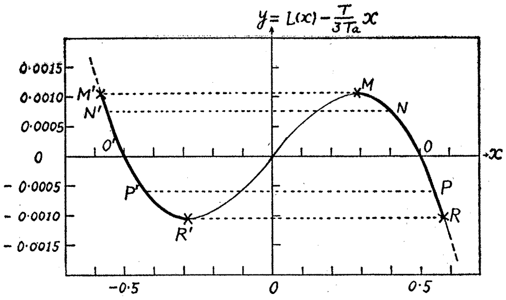

FIG. 6. The ordinate represents $L(x)-\frac{1}{3}(T/T_a)x$, for a temperature $T/T_a=0.9837$. The sets of points such as OO', PP', and so on satisfy Eq. (51). Antiferroelectric solutions can exist only between two horizontal lines MM' and RR'.

Two characteristic points may be noted: The D-E curve show a slight upward curvature, in contradistinction to the well established downward curvature in ferroelectric D-E curves. The antiferroelectric D-E curve can exist only between the two limits, M and R, and if the field should exceed this threshold value the crystal would be forced to make a transition to another type of phase; of course this forced transition would be observed only when the crystal happens to be strong enough to bear a sufficiently intense field.

Whether this other phase to which the crystal is to make a forced transition is ferroelectric or paraelectric, depends entirely upon whether the given temperature T

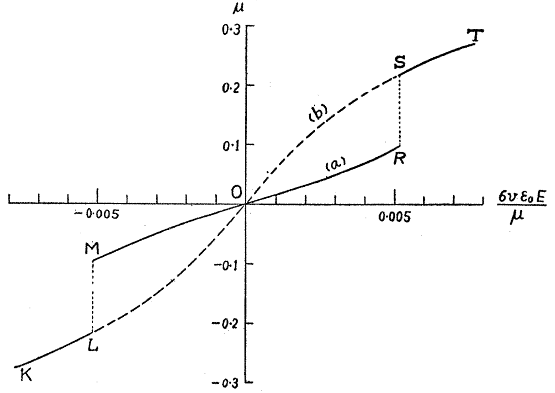

FIG. 7. The ordinate represents $L(x_1)+L(x_2)$, which is proportional to net dipolar polarization (see Eq. (14)) (a) for antiferroelectric phase at $T/T_a=0.9837$, (b) for paraelectric phase at $T/T_f=1.016$. If for a crystal $K_0=100$ and $K_c=3200$, then these two reduced temperatures correspond to the same actual temperature, and the P_d-E curve should go successively through the points K-L-M-O-R-S-T.

is higher or lower than the value of T_f expected for the crystal concerned, and this is determined by what we choose for the values of K_0 and K_c, so that the D–E curves of another phase can have great variety of form. For example, if we assume that $K_0=100$ and $K_c=3200$, the given temperature T turns out to be higher than T_f, namely $T=1.0161T_f$, since the ratio of the two Curie points calculated by means of (44) is $T_f/T_a=0.9681$. Therefore, for this case, the other phase must be a paraelectric one.

The D–E curve for this paraelectric phase is also obtainable from Eq. (52), in which $x_1=x_2=x$ must be used. The result is shown plotted in the same figure.

Though it is certain that an antiferroelectric phase cannot persist outside of the limits M and R, yet these extreme points must not be regarded as representing true transition points between the two phases. It is in general expected from a thermodynamical point of view that the free energy curves for both phases will intersect at some points lying somewhere inside the extremities. However, after calculation in the present case, it has turned out that both the free energy curves seem, within the accuacy of our calculation, to intersect at the very ends of the antiferroelectric range, namely, just at M and R. We have shown this situation by the two vertical dotted lines in Fig. 7.

Besides, we have a proof for the statement given at the end of Sec. V that, for the paraelectric case, K should decrease with increasing dc bias. Indeed the curve (b) in Fig. 7 is clearly seen to have a remarkable downward curvature.

VII. TRANSVERSE APPLICATION OF FIELD

When the sublattices are spontaneously polarized in the direction of the z-axis, the crystal is no longer of cubic symmetry but is of tetragonal symmetry, so that the dielectric constant tensor will be completely determined if we know the dielectric constant in an arbitrary direction perpendicular to z-axis. We shall examine what results will be obtained if an external field is applied parallel to, say, the $+x$ direction.

The local fields then have x as well as z components; they can be written as

$$F_{ix}=E+\sum_{j=1}^{3} f_{ij}^{x}P_{jx}/\epsilon_0, \quad i=1,2,3, \tag{53}$$

$$F_{iz}=\sum_{j=1}^{3} f_{ij}P_{jz}/\epsilon_0, \quad i=1,2,3 \tag{54}$$

where the f_{ij} are the same as those previously introduced, while the f_{ij}^{x} are to be obtained, as before, from a paper by McKeehan;[7]

$$\begin{aligned} &f_{ij}^{x}=f_{ji}^{x},\\ &f_{11}^{x}=f_{22}^{x}=\tfrac{1}{3}-0.2130,\\ &f_{12}^{x}=\tfrac{1}{3}+0.2130,\\ &f_{13}^{x}=f_{23}^{x}=f_{33}^{x}=\tfrac{1}{3}. \end{aligned} \tag{55}$$

The polarizations are

$$\begin{aligned} &P_{\alpha ix}=\epsilon_0\alpha_1F_{ix}/2v, \quad P_{\alpha iz}=\epsilon_0\alpha_1F_{iz}/2v; \quad i=1,2\\ &P_{\alpha 3x}=\epsilon_0\alpha_3F_{3x}/v, \quad P_{\alpha 3z}=\epsilon_0\alpha_3F_{3z}/v, \end{aligned} \tag{56}$$

and

$$\begin{aligned} P_{dix}&=(\mu/2v)\int \sin\theta\cos\varphi\, n_i(\omega)d\omega,\\ P_{diz}&=(\mu/2v)\int \cos\theta\, n_i(\omega)d\omega, \quad i=1,2. \end{aligned} \tag{57}$$

Proceeding in a similar manner to that used in Sec. II, we get the most probable distribution functions,

$$n_i(\omega)=\frac{x_i}{4\pi\sinh x_i}\exp[x_i(\cos\theta_i\cos\theta+\sin\theta_i\sin\theta\cos\varphi)], \quad i=1,2, \tag{58}$$

where the four parameters x_i and θ_i are to be solved as the relevant roots of the following set of equations:

$$x_i\cos\theta_i/\sigma=\sum_{j=1}^{2} g_{ij}\cos\theta_jL(x_j), \quad i=1,2, \tag{59}$$

$$x_i\sin\theta_i/\sigma=h^{x}(2v/\mu)\epsilon_0E+\sum_{j=1}^{2} g_{ij}^{x}\sin\theta_jL(x_j), \quad i=1,2, \tag{60}$$

where h^x and g_{ij}^{x} are the coefficients composed of α_i and f_{ij}^{x} in a similar manner to that used in Sec. II.

In an antiferroelectric case, we get at once

$$x_1=x_2=x, \quad \theta_1=\Theta=\pi-\theta_2,$$

and accordingly

$$x/\sigma=(g_{11}-g_{12})L(x), \tag{61}$$

$$\sin\Theta=\{h^{x}(2v/\mu)\epsilon_0E\}/\{[(g_{11}-g_{12})-(g_{11}^{x}+g_{12}^{x})]L(x)\}. \tag{62}$$

We see from (61) that the $x-T/T_a$ relation is not influenced at all by a transverse application of any external field whatever. The dipolar polarizations calculated by means of (57) and (58) turn out to be, for this solution.

$$\begin{aligned} P_{d1x}&=P_{d2x}=(\mu/2v)L(x)\sin\Theta,\\ P_{d1z}&=-P_{d2z}=(\mu/2v)L(x)\cos\Theta. \end{aligned} \tag{63}$$

This tells us that the axes of cylindrical distribution of the dipole orientations are both rotated away from their original directions toward the $+x$ direction by the angle Θ given in (62).

Substituting these polarizations into the electric displacement,

$$D_x=\epsilon_0E+\sum_{i=1}^{3} P_{ix},$$

we obtain

$$D_x=\left[1+\frac{(\alpha_1/v)+(\alpha_3/v)}{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)}+\frac{1}{1-\frac{1}{3}(\alpha_1/v+\alpha_3/v)}\right.$$
$$\left.\times\frac{h^x}{(g_{11}-g_{12})-(g_{11}{}^x+g_{12}{}^x)}\right]\epsilon_0 E. \quad (64)$$

We see at once that K_x is independent of temperatures, because the terms in the bracket are all composed of only constant quantities. And since it is easily proved that

$$g_{11}{}^x+g_{12}{}^x=g_{11}+g_{12}, \quad (65)$$

$$h^x=h \quad (66)$$

this constant value of K_x turns out to be just equal to the value of K_c previously found for the dielectric constant at the Curie point.

In the ferroelectric case, however, we find a rather undesirable result; K_x turns out to be infinite at all temperatures below the critical point. But this result is consistent with the fact that K_c is really infinite for ferroelectric cases.

VIII. DISCUSSIONS

So far we have shown that a CsCl type crystal containing rotatable polar molecules can show either ferroelectric or antiferroelectric properties depending solely upon the values of the polarizabilities of its components. In addition, we have examined in what respects the two phases will be able to show contrasts of phenomenological importance, and in what respects they will behave very similarly notwithstanding the essential difference in their dipole configurations.

As is clearly seen, we have hitherto been discussing merely the theoretical possibilities to be derived from our hypothetical model, though of course with the hope that the results obtained would be of some use in interpreting the dielectric properties of some actual crystals. Now let us examine what modification must be introduced when some other model is considered.

Careful inspection of the present theory tells us at once that, so long as a crystal really contains rotatable dipoles and so long as a decomposition of the dipole lattice into a set of two sublattices is allowable from the first as in the present model, the general aspects of the theoretical predictions should remain valid however complicated the crystal structure may be. Of course, then the factors such as h and g_{ij} will become more complicated and some of the results such as shown in Figs. 2 and 4 may be changed very considerably, while some other predictions such as those presented in Eqs. (18), (23), (27), (38), and also in Eqs. (49) and (50) will be valid in just the same forms.

Also, even when a crystal contains dipoles due to the finite shift of ions on a specified line instead of freely rotatable polar molecules, as perhaps is the case with some actual crystals like rochelle salt, most of the fundamental equations will be retained, except that Eqs. (3) and (4) should be replaced by

$$P_{di}=(\mu/2v)[n_i(+)-n_i(-)], \quad (67)$$

$$S=k\sum_{i=1}^{2}\log\frac{[n_i(+)+n_i(-)]!}{n_i(+)!n_i(-)!}, \quad (68)$$

where $n_i(+)$ and $n_i(-)$ denote the number of the dipoles on lattice i in the directions $+z$ and $-z$, respectively. Then all the Langevin functions, wherever they may appear, will be replaced by another similar function tanh$x$, or $L_{\frac{1}{2}}(x)$, as is at once expected from an analogy to the Weiss-Heisenberg theory of scalar spin ferromagnetism and antiferromagnetism.[9] Most of the theoretical predictions, except those concerning the form of the specific heat curve, will, however, again remain valid, at least qualitatively.

Since last year we have been investigating the dielectric properties of ceramic $PbZrO_3$. Its dielectric constant-temperature curve resembles that of the well-known ferroelectric $BaTiO_3$ so much that it has been suggested that $PbZrO_3$ might also be a kind of ferroelectric.[10]

After our detailed investigation, however, we have found:[11]

(i) Its dielectric constant increases slightly with increasing dc bias below the Curie point, while it decreases with increasing bias above the Curie point.

(ii) Its D–E curves observed on a cathode-ray oscilloscope show a slight upward curvature just below the Curie point, and moreover when the amplitude of the applied alternating field is greater than 30 kv/cm at 226°C, an impressive form of queer D–E curve is seen, very similar to that shown in Fig. 7, with abrupt increases of polarization on both ends.

We inferred, therefore, that this material might rather be an antiferroelectric, though its actual structure was unknown at that time. In the meantime, this surmise has proved to be true. Indeed, very recently, Sawaguchi, Maniwa, and Hoshino[12] have succeeded in proving by means of an x-ray analysis of single crystals of $PbZrO_3$ the existence of an essentially antiferroelectric dipole arrangement in a plane perpendicular to its c-axis, though the question whether it can be slightly ferroelectric in c-direction has been left open. Roberts has subsequently measured the piezoelectric effect of this material and has found that it certainly exists, though it is in fact very small.[13]

Considering these events, it seems reasonable to suggest that most of the theoretical predictions may be valid also for more general types of crystals, though of

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course qualitatively, even when their accurate structures are not known initially.

The most undesirable prediction derived from our theory may probably be that concerning the transverse dielectric constant; that is, K_x is far larger than is reasonable. But it is certain that this defect has arisen chiefly because no crystal anisotropy whatever is taken into account. If a crystal is spontaneously polarized in any one direction, there is no reason at all why it must still be cubic. In general, the crystal would preferably become strained, since the strains would stabilize all the more the specified axis of dipole orientation. Any amount of rotation of the axis of polarization away from the easiest direction would be realizable only when the transverse field is strong enough to overcome the potential barriers surrounding the easiest axis; this effect will certainly diminish the K_x value considerably.

In this respect, it seems very interesting to notice that in single crystals of $BaTiO_3$, the dielectric constant in the direction perpendicular to its spontaneous polarization is found to be far larger than the dielectric constant measured in the parallel field.[14]

I wish to express my hearty thanks to the staff of our laboratory in the Tokyo Institute of Technology, especially to Messrs. T. Oguchi, G. Shirane, and E. Sawaguchi for their very helpful discussions.

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Interaction between the *d*-Shells in the Transition Metals. IV. The Intrinsic Antiferromagnetic Character of Iron

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The principles developed in the previous papers of this series are applied to interpret the presence of ferromagnetism in b.c.c. iron, its absence in f.c.c. iron. It is found necessary to introduce a new principle, namely that for minimum energy the *d*-shell electrons are distributed among the atoms so as to maximize the total number of pairs of electrons having like spin within the individual atoms. This principle leads to the viewpoint that, at least on a local scale, the b.c.c. iron lattice consists of the superposition of two interpenetrating simple cubic lattices of atoms having *d*-shell spins of different magnitudes and of opposite direction. The same principles lead directly to the observed saturation magnetizations of all iron base alloys.

I. INTRODUCTION

IN the previous papers[1] of this series the author has proposed that for the transition elements the magnetic structure of the *d*-shells of the individual atoms is essentially the same in the metallic as in the gaseous state, that ferromagnetic coupling between the incomplete *d*-shells in metals arises from an indirect coupling via the conduction electrons, and that the direct interaction between these shells is antiferromagnetic. These proposals have provided an unforced interpretation of the occurrence of ferromagnetism in the periodic table, of the occurrence of b.c.c. lattices in the transition metals, and have provided a quantitative calculation of the Weiss coupling factor. The essential validity of these proposals has been further strengthened by the observation of the antiferromagnetic behavior of the magnetic susceptibility of chromium by McGuire and Kriessman,[2] by the observation of the anomalously low value of the electronic specific heat of chromium at low temperatures by Friedberg,[3] by the computation of the binding energy of tungsten by Hsu,[4] by the analysis of the elastic constants of tungsten by Isenberg,[5] by the analysis of the Heusler alloys by Heikes,[6] and by the detailed analysis of the magnetic properties of alloys by Carr[7] in a forthcoming paper. Slater[8] has correlated the more usual band viewpoint with the atomistic viewpoint adopted in this series. In the second paper of this series it has been pointed out that, in the absence of *s* electrons, electrical conductivity by *d* electrons can also introduce ferromagnetic coupling. This relation between electrical conductivity by *d* electrons and ferromagnetic coupling has recently received further support from observations upon the ferrites. Below their Curie temperature a second critical temperature, or narrow temperature range, is found in which both the magnetic properties and the electrical conductivity suffer large abrupt changes. (Manganese ferrite,[9] iron

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