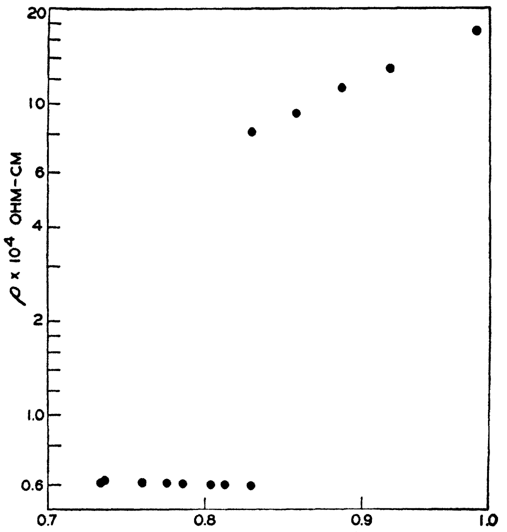

FIG. 1. Resistivity of germanium at high temperatures. The values for the resistivity of the solid are in good agreement with values obtained by extrapolating the direct current resistivity measured at lower temperatures.

The resistivity of the liquid germanium near the melting point was found to be 60×10^{-6} ohm-cm and the temperature coefficient of resistivity was found to be positive and about 1 or 2×10^{-4} (deg C)$^{-1}$. A synthesis of data from several runs is shown in Fig. 1.

The melting of germanium thus shows a certain analogy to the transition from gray, semiconducting tin to white, metallic tin at 13°C. In the case of tin there is a 20 percent increase in density and an increase of the coordination number from four to six as the temperature is raised through the transition, and recent work[5] has shown that the resistivity decreases by a factor of 16. Estimates of the density of liquid germanium by the author based on Hendus' data give a density increase of about 20 percent in germanium upon melting, and the conductivity measurement shows that the resistivity of the solid germanium at the melting point is fifteen times that of the liquid.

The author is indebted to Dr. A. W. Lawson for encouragement and advice. Since the start of these experiments it has come to his attention that independent work on the same subject is being carried on by A. Epstein and Dr. K. Lark-Horovitz at Purdue University.

* The investigations described were actually carried out in the laboratories of the Institute for the Study of Metals.

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Local Fields in Ionic Crystals*

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THE polarization of ionic crystals can consist of two parts. One part, the electronic polarization, arises from the polarization of the electronic distributions of the individual ions. The other part, the ionic polarization, arises from the displacement of the entire ions from their original positions in the lattice. When only electronic polarization is present, the local fields are found by replacing the electronic polarization with point dipoles at the lattice points. It has been customary in cases in which ionic polarization is also present to adopt a similar procedure. In this procedure the electronic and ionic polarizations are replaced with point dipoles at the original lattice points and the local fields at the original lattice points are found. However, the use of the local fields at the original lattice points is inconsistent with ionic crystal theory and can lead to large errors. In ionic crystal theory the local fields at the nuclei of the ions must always be taken as the effective polarizing fields for both electronic and ionic polarization. Consequently the local fields at the displaced positions of the ions must be used when ionic polarization is present.

The difference between the local field at the original and that at the actual position of an ion may be of the same order of magnitude as either local field. To understand this qualitatively, consider a crystal AB in which the lattice A has undergone a small homogeneous displacement. The usual procedure for finding the local field for an A ion includes contributions at the original lattice point from "equivalent dipoles" on A. Actually, since A has only suffered a uniform translation, it will give no contribution to the local field at an A ion. The field on A results from the displacement of B relative to A. In calculating this field the equivalent dipoles should be put on B rather than on A. Thus, putting the dipoles on A may lead to significant errors in the local field.

For simplicity we omit explicit consideration of the contribution of the electronic polarization to the local field. The ionic contribution to the local field at the actual position of the ith ion is given by

$$\mathbf{E}_i=\Sigma_j'(z_je\mathbf{r}_{ij})r_{ij}^{-3}, \tag{1}$$

where z_je is the charge of the jth ion and z_j its valence, and where the summation extends over all ions except the ith. $\mathbf{E}_i$ vanishes for a crystal in which each lattice point is a center of charge, that is, in which there is no ionic polarization. Suppose that each sublattice of such a crystal experiences a small homogeneous displacement from its original position in the lattice relative to some one of the sublattices. The ionic polarization of the lth sublattice produced by its displacement $\mathbf{d}_l$ is $\mathbf{P}_l=n_lz_le\mathbf{d}_l$, where n_l is the number of ions per unit volume on the lth sublattice. The separation between ions is now $\mathbf{r}_{ij}=\boldsymbol{\varrho}_{ij}-(\mathbf{d}_j-\mathbf{d}_i)$ where $\boldsymbol{\varrho}_{ij}$ is their separation in the original lattice. The right side of (1) can now be expanded to first order in the displacements, yielding

$$\mathbf{E}_i=\Sigma_j'\{3z_je[(\mathbf{d}_j-\mathbf{d}_i)\cdot\mathbf{r}_{ij}]\mathbf{r}_{ij}-z_je(\mathbf{d}_j-\mathbf{d}_i)r_{ij}^2\}r_{ij}^{-5}. \tag{2}$$

The right side of (2) can be converted into a sum over sublattices:

$$\mathbf{E}_k=\Sigma_l'f_{kl}\mathbf{P}_l+g_k\mathbf{P}_k, \tag{3}$$

where

$$g_k=-\Sigma_l'f_{kl}(n_lz_l/n_kz_k). \tag{4}$$

Only those crystal structures will be considered for which the f_{kl} are simply constants, the dipole field constants of the original lattice. Equation (3) gives the local field at the actual position of the ion when ionic polarization is present. The first term in (3) is the contribution of the ionic polarization of all sublattices except the kth. It can be represented as due to equivalent dipoles at the original positions of these sublattices. The second term in (3) is the contribution of the ionic polarization of the kth sublattice itself. As shown by (4) this contribution can be interpreted as due to appropriate equivalent dipoles at the original lattice points of the other sublattices.

Taking the local field at the original position of the ion is equivalent to neglecting $\mathbf{d}_i$ in (2). One would then have obtained $\mathbf{E}_k=\Sigma_lf_{kl}\mathbf{P}_l$. The difference between the two local fields is $(g_k-f_{kk})\mathbf{P}_k$. For sublattices for which $g_k=f_{kk}$, they are the same. The simplest crystals for which this is so are those with the NaCl structure and those with the CsCl structure. For many crystal structures, however, g_k-f_{kk} is of the same order of magnitude or greater than f_{kk} for one or more ions. The usual treatment of situations in which ionic polarization occurs must then be replaced by one in which the ionic polarization is dealt with explicitly. In particular, if only one sublattice has appreciable ionic polarization, a polarization equation for this ionic polarization must also be included in the treatment of the dielectric properties of the crystal. Calculations of this nature for $BaTiO_3$ are discussed in the following letter. In general, when more than one sublattice has appreciable ionic polarization, considerations similar to those used to obtain the local field must be used to obtain the elastic restoring forces on an ion. The ionic polarization equations should be

$$\mathbf{E}_k=\Sigma_l\beta_{kl}\mathbf{P}_l, \qquad (5)$$

where the local field $\mathbf{E}_k$ includes the electronic contribution and where the β_{kl} are related to the noncoulomb forces within the crystal.

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Ferroelectricity *versus* Antiferroelectricity in Barium Titanate*

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SLATER'S recent treatment of BaTiO$_3$[1] has shown that the probable origin of the ferroelectricity of BaTiO$_3$ and similar substances of perovskite structure is the strong dipole-dipole interaction within lines of O and Ti ions parallel to the spontaneous polarization. Slater found that the value of the ionic polarizability necessary for spontaneous polarization of the Ti ion alone is 0.947×10^{-24} cc. This value was checked here (see row 1, Table I).

Qualitative considerations suggest that the dipole-dipole interactions in BaTiO$_3$ might be stronger in an antiferroelectric state[2] than in the observed ferroelectric state, just as in the simple cubic structure. Consequently a treatment of BaTiO$_3$ similar to that of Slater was carried out for an antiferroelectric state to determine the ionic polarizability necessary for spontaneous antiparallel polarization.

The O ion on the y-z face of the unit cell will be designated as O$_x$ and similarly for O$_y$ and O$_z$ as shown in Fig. 1(A). The antiferroelectric state considered is one with polarization in a Z_5 array (in the notation of Luttinger and Tisza[3]), Fig. 1(B), on the Ti and O$_z$ sublattices, and with no polarization on the O$_x$, O$_y$, and Ba sublattices. For convenience, the Ti and O$_z$ ions will be referred to as 1 and 2, respectively. The only nonzero field constants for this arrangement are $f_{11}=f_{22}=5.351$ and $f_{12}=33.118$. The value of f_{12} was calculated by the Ewald method. The electronic polarizabilities used were those given by Slater.[1] The edge of the unit cell was taken as 4.00A.

Calculations were made assuming that Ti or O$_z$ alone contributes ionic polarization. The local fields at the original lattice points were used, as has been customary. However, as pointed out elsewhere in this issue,[4] the local fields at the displaced lattice points should have been used. The calculations were repeated using the local fields given by Eqs. (4) and (5) of reference 4. For the ferroelectric arrangement $g_2=47.013$, enhancing the local field at the O$_z$ ion considerably. On the other hand, $g_1=f_{11}=4\pi/3$. Hence the calculated polarizability is the same for Ti with both methods. For the antiferroelectric arrangements $g_2=66.236$ and $g_1=16.559$, enhancing the local field at both ions. The results of the calculations are given in Table I.

In general, the greater the local field and the greater the electronic polarizability of the ion contributing most to the local field, the smaller the ionic polarizability required for spontaneous polarization. When the local fields at the original lattice points are used, the results for ferro- and antiferroelectricity are the same for Ti. For O$_z$ less ionic polarizability is required for antiferroelectricity and hence antiferroelectricity is favored. In the actual crystal, however, both ions may contribute ionic polarization.[5] Since Ti requires less polarizability than O$_z$ in both arrangements, one would expect the Ti ion to contribute most of the ionic polarization. Hence, one cannot interpret decisively the favoring of ferroelectricity in BaTiO$_3$ with simple dipole-dipole interactions alone if the local fields are taken at the original lattice points. When the local fields at the actual lattice points of the ions are used, antiferroelectricity is favored for the Ti and the O$_z$ ions both. Thus even if one uses local fields at the actual lattice points, one still cannot explain the favoring of ferroelectricity in BaTiO$_3$ with the simple dipole-dipole interaction model.

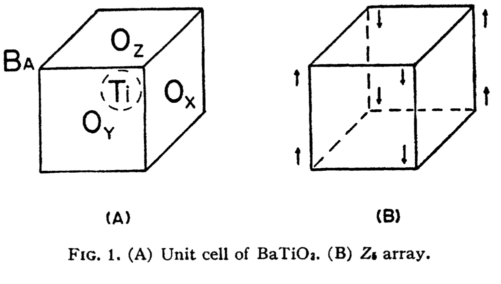

FIG. 1. (A) Unit cell of BaTiO$_3$. (B) Z_5 array.

TABLE I. Ionic polarizability required for spontaneous polarization.

Type of array	Local field	Ion displaced	Polarizability cc
1. ferroelectric (f.e.)	at original position	Ti	0.947×10^{-24}
2. antiferroelectric (a.f.e.)	at original position	Ti	0.947
3. f.e.	at original position	O$_z$	3.01
4. a.f.e.	at original position	O$_z$	5.06
5. f.e.	at displaced position	Ti	0.947
6. a.f.e.	at displaced position	Ti	0.787
7. f.e.	at displaced position	O$_z$	0.646
8. a.f.e.	at displaced position	O$_z$	0.626

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Angular Correlation in Magnetic Fields

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THE angular correlation of two successively emitted nuclear particles can be influenced by magnetic fields (e.g., from the electron shell, from neighboring atoms, or from an external source). In order to calculate a general expression, we start with the formula of Goertzel[1] for the emission probability W of two particles with directional vectors $\mathbf{k}_1$ and $\mathbf{k}_2$.

$$W(\mathbf{k}_1,\mathbf{k}_2)=S_1S_2\sum_{lmm'p}(A_l|H_1|B_m)(B_m|H_2|C_p)^*\times(A_l|H_1|B_{m'})^*(B_{m'}|H_2|C_p)\frac{1}{1-i\omega_{BB'}\tau}. \qquad (1)$$

A_1, B_m, C_p are the wave functions of the atom (nucleus+shell) for the 3 states of the cascade. H_1, H_2 designate the hamiltonians responsible for the emission of the first and second particles, respectively. $\omega_{BB'}$ is the energy splitting of the two levels B_m, $B_{m'}$, divided by $\hbar$. τ is the mean life of the intermediate state. We can now modify Goertzel's expression (1) by choosing an arbitrary z-axis. Introducing solid harmonics $Y_k^r(\mathbf{k})$ we get instead of (1)

$$W(\mathbf{k}_1,\mathbf{k}_2)=\sum_{r,k}G_k^rA_k\frac{1}{2k+1}Y_k^r(\mathbf{k}_1)Y_k^r(\mathbf{k}_2)^*. \qquad (2)$$

As is seen later, the coefficients a_k are independent of the magnetic field. The whole influence of the magnetic field is in fact contained in the attenuation factor G_k^r. This attenuation factor can be calculated for the two special cases of a weak and strong field.