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Polarizabilities of Ions in Perovskite-Type Crystals

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Each type of ion is shown to have very nearly the same polarizability in different crystals of the perovskite type as well as in the diagonal cubic types reported previously. This conclusion is based on dielectric constant data for several titanates and zirconates and $KMgF_3$. The values of ionic polarizability are roughly proportional to the cube of the radius for ions in the same valence series.

I. INTRODUCTION

IN recent papers[1,2] the author proposed a theory of dielectric constants of simple crystals essentially based on the following familiar postulates:

(1) The electric field tending to polarize a given ion is that at its center produced by conditions external to the given ion.

(2) The induced electric moment of a given ion acts on other ions in the crystal like a central point dipole.

At frequencies low enough to avoid inertia effects, and at low field strengths, the ratio of the effective dipole moment to the polarizing field is constant for a given ion in a given crystal. This constant ratio is called the dielectric polarizability. In order to clarify the distinction between the polarizability as here defined and the very different but more usual concept of electronic or optical polarizability, a further discussion is given in Appendix I.

On the basis of dielectric constant data of a large number of compounds, it was shown[1] that the polarizability of each type of ion is very nearly the same in different crystals—subject to certain symmetry requirements. The criterion for testing this condition was the additivity relation:

$$\alpha = \sum \alpha_i, \tag{1}$$

where $\sum \alpha_i$ is the sum of the polarizabilities of all ions in the molecule or chemical formula, and α is calculated as follows:

$$\alpha = 3V(K-1)/(K+2), \tag{2}$$

where V is the volume per molecule or chemical formula, and K is the dielectric constant. Equation (1) is rigorous only when applied to crystals of "diagonal cubic" symmetry, such as NaCl, CsCl, CaF_2, and cubic ZnS, but not to perovskite-type crystals. Nevertheless, it does appear to "work" deceptively well when applied to certain titanates of the perovskite-type. The value of K employed in Eq. (2) should be determined under symmetry conditions such that the static local field tending to polarize each ion is zero and its electric moment vanishes.

A detailed analysis of perovskite-type crystals and barium titanate in particular was given by Slater,[3] making implicit use of the postulates mentioned above. Slater apparently did not accept the conclusion that the polarizability of a given ion is very nearly the same in different crystals. He allowed only that the polarizability of the titanium ion is "not larger in order of magnitude than that usually found." His treatment actually implied that the looseness of the titanium ion should have a dominant effect on its polarizability in barium titanate. This looseness arises because the space available for titanium in the middle of an oxygen octahedron is slightly too large. Titanium was then treated as though it had special properties not shared by other ions.

In the following discussion it will be shown that Eq. (1) is valid to a rough approximation even in barium titanate in which the detailed picture is much different than that used in deriving (1). It will also be shown that the polarizability of titanium is substantially the same in strontium titanate, in which no excess space is available. It will likewise be shown that the ferroelectric nature of lead zirconate can be satisfactorily explained by reasonable values of the polarizability of zirconium and lead which agree with other data. In addition, the newly reported dielectric constants of $KMgF_3$ and $BaZrO_3$ will be shown to be consistent with the present theory.

II. EXPERIMENTAL EVALUATION OF POLARIZABILITIES

Dielectric constants and unit cell volumes of the perovskite crystals being considered are shown along with similar data for a number of diagonal cubic crystals in Table I. This table indicates a new value, 34±3, for the dielectric constant of BaO, which was obtained by Sproull and Bever of Cornell University.[4] This result appears to be well substantiated although it is very different from the value previously supposed. It has therefore been necessary to re-evaluate the polarizabilities of the alkaline-earth and oxygen ions in order to be consistent with this result.

The negative values of dielectric constant quoted for

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[1] S. Roberts, Phys. Rev. 76, 1215 (1949).

[2] S. Roberts, Phys. Rev. 77, 258 (1950).

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

[4] Private communication; also mentioned in oral presentation by R. L. Sproull, Phys. Rev. 75, 1282 (1949).

TABLE I. Experimental data and polarizabilities.

	(1) K	(2) V (A³)	(3) α (A³)	(4) $\Sigma\alpha_i$ (A³)
MgO	9.8	18.52	41.4	43.0
CaO	11.8	27.65	64.9	66.9
SrO	13.3	33.16	79.9	81.1
BaO	34	41.59	114.4	108.8
CaF_2	8.43	40.47	86.5	84.5
SrF_2	7.69	48.27	99.9	98.7
BaF_2	7.33	59.29	120.8	126.4
$SrTiO_3$	295	59.54	176.8	160.1
$BaTiO_3$	−1860	64.36	193.3	187.8
$BaZrO_3$	43	73.51	205.7	191.8
$PbZrO_3$	−950	71.00	213.6	206.5
$KMgF_3$	8.5	63.04	135.1	127.8

$BaTiO_3$ and $PbZrO_3$ correspond to the unstable cubic form and are obtained from published data[5] by extrapolating the Curie-Weiss law, valid in the cubic region, down to 25°C. The values of dielectric constant of $SrTiO_3$ and $BaZrO_3$ were determined on ceramic specimens and include a correction for porosity. The dielectric constant of $KMgF_3$ was estimated (8.5 ± 0.5) by S. I. Reynolds of this laboratory by examining the motion of small crystal grains in carefully dried dielectric liquids of various dielectric constants, while applying a non-uniform electric field.

The calculation of the cell volume of the titanates and zirconates is based on the measurements of Megaw,[6] while that of $KMgF_3$ is determined from the value $a_0=(3.980\pm0.002)$A measured by B. F. Decker of this laboratory.

The third column in Table I shows the polarizability in cubic angstroms, calculated from the dielectric constant and unit cell volume by means of Eq. (2).

A revised list of the dielectric polarizabilities of ions is shown in Table II. The values for halide ions are taken directly from reference 1, and those for the alkali ions are modified only slightly so as to be in better agreement with reference 2. The polarizabilities of the alkaline earth ions and oxygen are adjusted to a somewhat greater extent in order to comply with the new result for barium oxide. Values for titanium and zirconium are averages of the results calculated in this paper. The polarizability of lead is uncertain, since it was determined from dielectric constants of crystals (PbO, $PbCl_2$, and PbI_2) which lack diagonal cubic symmetry.

The sums of the appropriate ionic polarizabilities shown in Table II are calculated for each of the various compounds of Table I and are shown in the fourth column of that table. These values are in satisfactory agreement (five percent tolerance) with the results shown in column three for the diagonal-cubic crystals. The use of Eq. (1) evidently introduces a somewhat larger error in estimation of the values of α in perovskite-type crystals, although the difference could be much greater in more extreme cases.

TABLE II. Dielectric polarizabilities of ions in cubic angstroms.

Li^+	11.7	Mg^{++}	9.0
Na^+	19.7	Ca^{++}	32.9
K^+	41.4	Sr^{++}	47.1
Rb^+	57.3	Ba^{++}	74.8
Cs^+	71.5	Ti^{+4}	11.0
F^-	25.8	Zr^{+4}	15.0
Cl^-	62.8	$O^=$	34.0
Br^-	81.0		
I^-	109.4	Pb^{++}	(89.5)

III. CALCULATED RESULTS FOR PEROVSKITE CRYSTALS

A more accurate and more detailed treatment of perovskite crystals is that considered by Van Santen and Opechowski,[7] and more recently by Slater.[3] The mathematical details of this treatment are summarized in Appendix II.

By this method a different field constant, β_i, is calculated for each ion signifying the ratio of the actual field acting on the given ion to the Lorentz internal field, $F=E+P/3\epsilon_0$. The polarizabilities of the various ions are likewise designated by numerical subscripts, α_2 being the polarizability of titanium or zirconium. The values of α_2 are calculated by making use of the given values of α and the polarizabilities of the other ions as listed in Table II. The resulting values of α_2 and the internal field constants β_i are shown in Table III.

Table III indicates a slightly smaller polarizability for Ti in $SrTiO_3$ than in $BaTiO_3$. Such a difference is not inconsistent with the approximate nature of the theory; however, it may also be attributed to considerations such as those outlined by Slater. In any event, the small difference indicates that looseness of the titanium ion is not the dominant factor controlling its polarizability in barium titanate. It may also be noticed that a similar difference is observed in the polarizability of zirconium in $BaZrO_3$ and $PbZrO_3$, although there is no question of "looseness" in either.

The values of the field constants in each of the compounds of Table III show that there is a strong interaction between the ions in the sites corresponding to titanium and its oxygen neighbor in the field direction. Lead zirconate is strikingly different from the others in that the corresponding ions are polarized in reverse to the normal internal field direction. This fact may attempt to explain some of the differences in structure and properties of lead zirconate as compared with barium titanate. For example, the observation that the tetragonal unit cell, or pseudo-cell as the case may be, of lead zirconate has an axial length shorter than its lateral

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[5] S. Roberts, J. Am. Ceram. Soc. 33, 63 (1950).

[6] H. D. Megaw, Proc. Phys. Soc. (London) 58, 133 (1946).

[7] J. H. Van Santen and W. Opechowski, Physica 14, 545 (1948).

dimensions, or $c_0/a_0<1$, while barium titanate, to the contrary,[6] has $c_0/a_0>1$, may be related to this internal field reversal and to the relatively greater total polarization of the remaining ions.

The values calculated for α_2 in the above manner do not depend too critically on the choice of the polarizabilities of the other ions. For example, Slater[3] in calculating the polarizability of titanium in barium titanate used the author's[1] former published value 30.0 for the polarizability of oxygen and a surprisingly low value, 24.42, for the polarizability of barium. Even so, his result for titanium was only 14.26 as compared with our value of 12.1. On the other hand, the internal field constants β_i are very sensitive to small changes in the values of α_i. For this reason, not too much reliance should be placed on the specific values of β_i shown in Table III.

It is instructive to compare the polarizabilities of ions *versus* their radii. Figure 1 shows such a comparison for the ions listed in Table II. Two values of radius are indicated in this figure, namely, those due to Pauling, by crosses, and those due to Goldschmidt, by circles. The values are taken from a table on p. 268 of the book by Mott and Gurney.[8] For ions of equal valence the polarizability is roughly proportional to the cube of the radius, or to the volume. There are definite exceptions to this rule of the same order of magnitude as the differences between the two values of the radii.

IV. CONCLUSIONS

Dielectric constants of all ionic crystals having diagonal cubic or perovskite symmetry appear to be consistent with an interpretation based on the following considerations.

(1) The electric field tending to polarize a given ion is that at its center produced by conditions external to the given ion.

(2) The electric moment of a given ion acts on other ions in the crystal like a central point dipole.

(3) The dielectric constant is determined under symmetry conditions such that the local field tending to polarize each ion is zero and its electric moment vanishes.

(4) The ratio of the electric moment to the polarizing field is a nearly invariant property of an ion, called its "dielectric polarizability." This value of polarizability is defined under conditions of constraint only by the neighboring ions. It is appreciably different from the "electronic polarizability," which involves restraint of the nucleus by its own inertia.

Several of the substances considered, namely, LiBr, LiI, and $BaTiO_3$, are thought to contain cations which are smaller than the available space. Nevertheless, the results indicate that this fact, if true, has no more than a minor effect on the polarizability of these ions.

TABLE III. Calculated polarizabilities and field constants.

	α_2 (Ti, Zr)	β_1 (Sr, Ba)	β_2 (Ti, Zr)	β_3 (O_x, O_y)	β_5 (O_z)
$SrTiO_3$	9.9	0.17	3.9	0.57	2.69
$BaTiO_3$	12.1	-2.14	11.9	-0.83	7.79
$BaZrO_3$	15.9	0.095	4.14	0.36	3.19
$PbZrO_3$	14.2	2.26	-3.33	1.84	-1.94
$KMgF_3$	11.0	0.76	1.82	0.80	1.64

APPENDIX I

In order to study the effect of an electric field on a single isolated ion, it is necessary to support the ion mechanically, since it has a net charge and experiences an electrostatic force. The electric moment is produced by the displacement of the charged particles constituting the ion relative to their zero-field positions. In a recent paper,[2] the author showed that the magnitude of the induced electric moment depends critically on how the ion is held. If it is held by restraining the motion of its external boundary, then the electric moment will generally be much greater than that produced if the nucleus instead is held fixed.

The restraint on the boundary corresponds to that imposed by adjacent ions on each other in a crystal. Evidence for such restraint can be found in the constancy of ionic radii in crystals. The restraint of the nucleus occurs when a free ion is placed in a field which oscillates so rapidly that the inertia of the nucleus effectively prevents it from moving. In this way it can be seen that the dielectric polarizability defined under the conditions of restraint of the boundary is appropriate for interpreting the dielectric constants of crystals and is, or may be, radically different

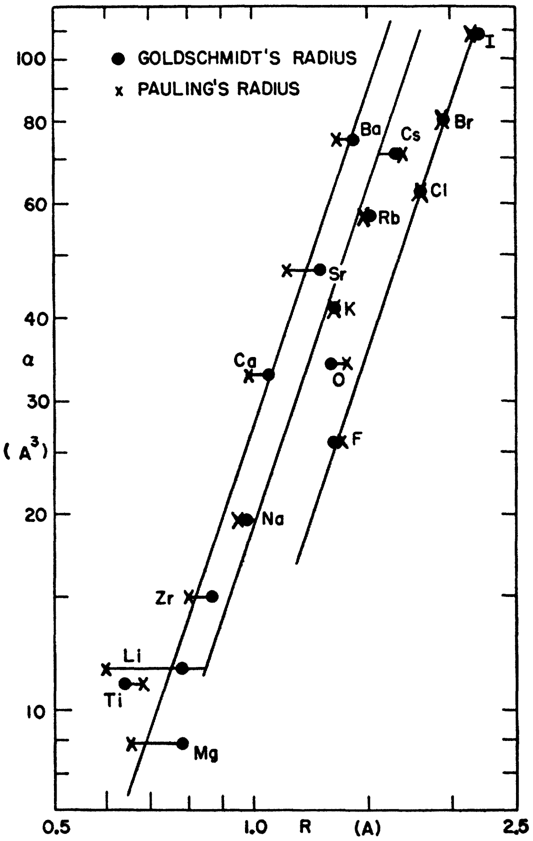

FIG. 1. Dielectric polarizabilities *versus* ionic radii.

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[8] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940).

from the electronic or optical polarizability defined under the conditions of nuclear restraint. The latter is valid for isolated ions measured at optical frequencies. The polarizabilities of ions in crystals at optical frequencies were shown to be even somewhat smaller than the electronic polarizabilities defined above, owing to the additional mutual restraint of their boundaries.

APPENDIX II

In diagonal cubic crystals, that is, in cubic crystals in which a rhombohedral unit cell can be constructed having all the ions on its diagonal, the local field acting on each ion is the same. It is

$$F_i = E + \Sigma\, P_j/3\epsilon_0 = (K+2)E/3, \tag{3}$$

where E is the external electric field, P_j is the dipole moment per unit volume of the jth ion, and ϵ_0 is the permittivity of space.

In perovskite-type crystals, a different field is effective for each ion, as distinguished by different values of β_i.

$$F_i = \beta_i(K+2)E/3. \tag{4}$$

In terms of the various components of polarization the local field at the ith ion is alternatively

$$F_i = E + (1/3\epsilon_0)\, \Sigma_j(f_{ij}+1)P_j, \tag{5}$$

where each f_{ij} is a matrix element calculated from the geometrical arrangement of the ions.

The numerical subscripts, 1 to 5, are assigned in the following order: Ba, Ti, O_x, O_y, and O_z, in which O_x is the oxygen ion having its nearest Ti neighbor in the x-direction, etc. If the electric field is applied in the z-direction, then the resulting matrix for f_{ij} is

$$(f_{ij}) = \begin{bmatrix} 0 & 0 & +1.0346 & +1.0346 & -2.0692 \\ 0 & 0 & -3.5908 & -3.5908 & +7.1816 \\ +1.0346 & -3.5908 & 0 & -2.0692 & +1.0346 \\ +1.0346 & -3.5908 & -2.0692 & 0 & +1.0346 \\ -2.0692 & +7.1816 & +1.0346 & +1.0346 & 0 \end{bmatrix}.$$

In calculation of the above matrix, values of $4\pi(f_{ij}+1)/3$ were taken from a paper by McKeehan[9] as determined by the method of Ewald.

Instead of Eq. (1), a different relation is valid between the macroscopic polarizability α and the ionic polarizabilities α_i:

$$\alpha = 3V(K-1)/(K+2) = \Sigma\, \alpha_i\beta_i = \Sigma\, \gamma_i, \tag{6}$$

in which the last equality is taken as a definition of γ_i. The values of γ_i are solutions of a series of simultaneous equations:

$$(1/\alpha_i)\gamma_i - \Sigma_j(f_{ij}/3V)\gamma_j = 1. \tag{7}$$

Equations (6) and (7) are then sufficient to replace Eq. (1) in calculation of the relation between the various polarizabilities in perovskite-type crystals.

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