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Dielectric Constants and Polarizabilities of Ions in Simple Crystals and Barium Titanate

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The observed dielectric constants of alkali halides and certain other types of crystals coincide with a relatively simple interpretation of dielectric polarization which is based on the classical equation of Clausius and Mosotti. The polarizability of each elementary ion has only a small positive temperature coefficient and is invariant when the given ion is incorporated in different crystalline solids subject to certain symmetry requirements. The polarizabilities of the ions in cubic barium titanate, although normal, account quite satisfactorily for the high observed values of dielectric constant. A method of estimating dielectric constants from the known polarizabilities of ions is applied to several compounds for which dielectric data have not been reported.

I. INTRODUCTION

The equation of Clausius and Mosotti,[1] relating the dielectric constant of a substance to the polarizability of the particles of which it is made has been known for a great many years and has been successfully applied to gases and non-polar liquids. The corresponding equation for optical index of refraction, attributed to Lorentz and Lorenz, has, in addition, been applied to simple ionic crystals of the alkali-halide type, but the results of this application were not originally viewed with satisfaction, since there were reported systematic deviations between theory and experiment.[2–4] This equation was later reviewed by Shockley[5] who found that values of polarizability could be assigned to individual ions in such a way that their sums coincided with the polarizabilities of compounds as calculated by the Lorentz-Lorenz formula. The deviations were found to be not greater than three percent.

The purpose of the present paper is to report the successful correlation of dielectric constants of ionic crystals by using the Clausius-Mosotti equation and to show in what types of crystals this relation may be expected to be valid. A brief résumé of the derivation of the fundamental equations is given. This is followed by a discussion of the experimental data in which polarizabilities of the individual ions are derived. The temperature coefficients of dielectric constant are analyzed, and it is shown that the polarizability changes only very slightly with temperature, even, as in barium titanate, when the temperature coefficient of dielectric constant is very high.

II. THEORY

The Clausius-Mosotti equation states a relation between the polarizability, α, per molecule of a substance and its dielectric constant K.

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

where V is the volume of the unit cell in the crystal lattice divided by the number of molecules which it contains. A corollary of the Clausius-Mosotti equation is that the polarizability of a molecule is equal to the sum of polarizabilities of the ions which it contains. Thus, in a diatomic molecule

$$\alpha=\alpha_1+\alpha_2=3V(K-1)/(K+2). \tag{2}$$

This cannot be verified directly by experiment, since neither α_1 nor α_2 can be measured independently. But it can be checked indirectly, since it leads to an additivity relation between polarizabilities of the different compounds AC, AD, BC and BD of the same elements A, B, C, and D. Thus:

$$\alpha_{AC}+\alpha_{BD}=\alpha_{AD}+\alpha_{BC}=\alpha_A+\alpha_B+\alpha_C+\alpha_D. \tag{3}$$

Jonker and van Santen[6] have already demonstrated a special case of additivity in the example of several titanates, in which $\alpha_{\mathrm{MO}}+\alpha_{\mathrm{TiO_2}}=\alpha_{\mathrm{MTiO_3}}$, M being an alkaline earth. We find that the experimental data not only confirm this result, but indicate that the more general additivity of separate ionic polarizabilities is valid to a good approximation in a large number of simple crystalline substances in accord with Eq. (3). On the other hand, this equation is not valid for a large number of less symmetrical crystals. These observations are consistent with a relatively simple theoretical interpretation.

The successful application of the additivity relation implies, first of all, that the total polarization, P, per unit volume (electronic and ionic) may be thought of as a sum of components of the form, P_i, each associated with a given ion, i. A definite non-linear relation may be conceived to exist between a given component P_i and the local field F_i which induces it. The analysis of the problem is greatly simplified by restricting its application to examples involving only relatively small values of F_i. If F_i is small enough, the relation between F_i and P_i may be represented by a linear approximation.

Fortunately, there are a great many compounds which crystallize in such a way that ions of one type are

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[1] O. F. Mosotti, Mem. di Math. e di Fisica in Modena **24** (II), 49 (1850). R. Clausius, Die Mechanische Warmetheorie **II**, 62 (Vieweg) (1879).

[2] K. Spangenberg, Zeits. f. Krist **57**, 494 (1923).

[3] K. Fajans and G. Joos, Zeits. f. Physik **23**, 1 (1924).

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

[5] W. Shockley, Phys. Rev. **70**, 105 (1946).

[6] G. H. Jonker and J. H. van Santen, Chem. Weekblad **43**, 672 (1947).

symmetrically arranged around ions of another type. In these crystals, the coulomb forces on a given ion are normally in a state of balance, a fact which corresponds to a zero value of the field F_i. In these crystals, the value of the field F_i depends only on the applied field E and the polarization which it induces. Since these field components can be small compared to the coulomb forces between neighboring ions, the linear approximation can be used for P_i and the constant ratio so defined is a measure of the polarizability α_i.

$$\alpha_i = VP_i/\epsilon_0 F_i, \tag{4}$$

where ϵ_0 is the permittivity of free space and V is the volume per molecule in the crystal lattice as determined by x-ray diffraction or density measurements.

Owing to saturation effects in crystals in which an ion is normally subjected to strongly unbalanced coulomb forces ($F_i \neq 0$), one might expect the derivative dP_i/dF_i to be less than the value $\epsilon_0\alpha_i/V$, obtained by differentiating Eq. (4). This is closely related to the "deformation" effect discussed by Fajans and Joos[3] in connection with electronic (optical) polarizabilities, and is consistent with the observed non-linear dielectric properties of barium titanate.[7]

TABLE I. Dielectric constant, molecular volume and molecular polarizability of electrically balanced crystals.

Compound	K	V	α	$\Sigma\alpha_i$
LiF	9.27	16.21A^3	35.7A^3	37.5A^3
LiCl	11.05	33.74	77.9	74.5
LiBr	12.1	41.36	97.6	92.7
LiI	11.03	54.00	124.7	121.1
NaF	6.0	24.65	46.2	46.0
NaCl	5.62	44.59	81.1	83.0
NaBr	5.99	52.95	99.3	101.2
NaI	6.60	67.46	131.7	129.6
KF	6.05	38.07	71.6	68.1
KCl	4.68	61.86	102.2	105.1
KBr	4.78	71.42	119.6	123.3
KI	4.94	87.67	149.4	151.7
RbF	5.91	44.85	83.6	83.9
RbCl	5.0	69.93	119.8	120.9
RbBr	5.0	80.50	137.9	139.1
RbI	5.0	98.30	168.4	167.5
CsCl	7.20	69.43	140.4	134.1
CsBr	6.51	78.95	153.2	152.3
CsI	5.65	94.94	173.2	180.7
MgO	9.8	18.52	41.4	41.4
CaO	11.8	27.65	64.9	64.9
SrO	13.3	33.16	79.9	79.1
BaO	14.4	41.59	102.0	100.6
CaF_2	8.43	40.47	86.5	86.5
SrF_2	7.69	48.27	99.9	100.7
BaF_2	7.33	59.29	120.8	122.2
$CaTiO_3$	165.0	54.8	161.5	160.4
$SrTiO_3$	275.0	59.55	176.5	174.6
$BaTiO_3$ (120°C)	5000.0	64.0	193.0	196.1
Cu_2O	10.5	38.44	87.8	84.4
CuCl	10.0	39.49	88.8	90.0
CuBr	8.0	45.83	96.2	108.2
Ag_2O	8.8	52.58	114.0	108.8
AgCl	12.3	42.67	101.0	102.2
AgBr	13.1	47.97	115.4	120.4
TlCl	31.9	56.36	154.0	152.9
TlBr	29.9	62.57	170.0	171.1

The local field F_i, effective in polarizing the ions in certain types of cubic crystals has been derived by Lorentz.[8]

$$F_i = E + P/3\epsilon_0. \tag{5}$$

His assumptions are appropriate for the so-called "diagonal cubic" crystals, including NaCl, CsCl, CaF_2 and ZnS. There is less theoretical support for the Lorentz value of the internal field in perovskite-type crystals, although the additivity relation is obeyed equally well by these. Since the Lorentz value of internal field is a necessary condition for deriving the Clausius-Mosotti equation, the success of the latter in interpreting the experimental results is cited as evidence that the Lorentz field is that which actually exists. No other value would give equally satisfactory results.

Since F_i is by definition the same for all ions, the total polarization P in symmetric crystals may be expressed in a way which involves only the sum of the polarizabilities ($\sum \alpha_i = \alpha$).

$$P = \sum P_i = \sum \frac{\epsilon_0 F_i \alpha_i}{V} = \frac{\epsilon_0 F_i \sum \alpha_i}{V} = \frac{\epsilon_0 F_i \alpha}{V}, \tag{6}$$

α is thus the polarizability per molecule, obtained by adding the polarizabilities of all the ions making up the molecule.

The molecular polarizability α can be determined directly from the measured dielectric constant, since

$$\begin{aligned} P &= \frac{\epsilon_0 F_i \alpha}{V} = \frac{\epsilon_0 \alpha E}{V} + \frac{\alpha P}{3V} = \frac{\epsilon_0 \alpha}{V - (\alpha/3)} E, \\ K &= \frac{D}{\epsilon_0 E} = 1 + \frac{P}{\epsilon_0 E} = \frac{V + (2\alpha/3)}{V - (\alpha/3)} = \frac{1 + 2\beta}{1 - \beta}, \end{aligned} \tag{7}$$

in which $\beta = \alpha/3V$. In the above equation, D represents the electric displacement and K is the dielectric constant ($K = \epsilon/\epsilon_0$). Equation (7) may be alternatively expressed in a form more easily recognizable as the Clausius-Mosotti equation.

$$\alpha = 3V\beta, \text{ where } \beta = (K-1)/(K+2). \tag{8}$$

III. DIELECTRIC CONSTANTS AND POLARIZABILITIES

Table I gives experimental values for dielectric constant and molecular volume for a number of crystals which meet the requirement that each ion shall have a symmetrical environment. These include six different

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[7] S. Roberts, Phys. Rev. **71**, 890 (1947).

[8] H. A. Lorentz, "Theory of Electrons," Note 55, 308 (1916)

TABLE II. Polarizabilities of ions (cubic angstroms).

F^-	25.8	(7)	Li^+	11.7	(4)
Cl^-	62.8	(8)	Na^+	20.2	(4)
Br^-	81.0	(8)	K^+	42.3	(4)
I^-	109.4	(5)	Rb^+	58.1	(4)
			Cs^+	71.3	(3)
$O^=$	30.0	(9)			
			Mg^{++}	11.4	(1)
Cu^+	27.2	(3)	Ca^{++}	34.9	(3)
Ag^+	39.4	(3)	Sr^{++}	49.1	(3)
Tl^+	90.1	(2)	Ba^{++}	70.6	(3)
			Ti^{+4}	35.5	(3)

crystal types, all cubic, represented by NaCl, CsCl, CaF_2, CuCl, Cu_2O and $SrTiO_3$, respectively. The list is not believed to be exhaustive, although all symmetric crystals were included for which dielectric data were available.

The dielectric data in Table I are mostly drawn from a table compiled by Hojendahl.[9] The values of Cu_2O and Ag_2O were reported in another paper[10] by Hojendahl. The data for the titanates are given as reported by Wainer,[11] while the value for barium oxide is taken from a paper by Jonker and van Santen.[6] In checking the original sources of information, one finds rather large discrepancies in some cases. This is perhaps due to the fact that some substances could be obtained in the form of single crystalline plates large enough for accurate measurements, while other substances had to be measured in the form of a powder, or pellets formed from compressed powder.

The molecular volume, shown in the second column of Table II, is calculated from the dimensions of the crystal unit cell as determined by x-ray diffraction. The data compiled by Wyckoff[12] are used in this calculation. The molecular volume may alternatively be calculated from the density. In the alkali halides, the two results agree within a tolerance of about two percent.

The third column of figures in Table I gives the molecular polarizability as calculated by means of Eq. (8).

Taking the alkali halides as an example, one finds that the experimental data agree with the additivity relation to a good approximation.

For instance:

$$\begin{array}{ll} \alpha_{NaCl}=81.4, & \alpha_{NaI}=131.5, \\ \alpha_{RbI}=169.0 & \alpha_{RbCl}=121.7 \\ \hline 250.4, & 253.2. \end{array}$$

The polarizabilities of individual ions cannot be determined directly from dielectric constant measurements, although a series of sums and differences of polarizabilities can be derived from Table I so as to establish relative values for the polarizabilities of the different ions. In order to fix the absolute scale, the polarizability of oxygen is arbitrarily set equal to 30. When this is done, it is found that the resulting polarizabilities of the halide ions are nearly proportional to their volume. The average values of polarizability of the individual ions as determined in this way from the molecular polarizabilities in Table I are given in Table II. The numbers in parenthesis indicate the number of compounds in Table I which contain the given ion. The last column in Table I gives the values of molecular polarizability as calculated by adding the ionic values. No attempt has been made here to separate the total polarizabilities into electronic and ionic components.

The two values indicated for molecular polarizability in Table I check within a tolerance of five percent in every case except cuprous bromide. This is believed to be within the limits of experimental accuracy in view of the different sources of dielectric data and the slight differences between measured densities and x-ray densities. The deviations are not systematic.

Only one measurement has been reported for the

TABLE III. Dielectric constant, molecular volume and molecular polarizability of electrically unbalanced crystals.

Compound	K	V	α		$\Sigma\,\alpha_i$
		A			
TiO_2 (rutile)	114.0	$29.2A^3$	$85.3A^3$		$95.5A^3$
anatase	31.0	33.7	92.2		95.5
brookite	78.0	30.2	87.2		95.5
$MgTiO_3$	18.0	52.5	133.8		136.9
PbO	25.9	44.0	117.8		121.8
$PbCl_2$	33.5	77.7	213.0		217.4
PbI_2	20.8	122.4	319.0		310.6
(assume $\alpha=$	91.8 for Pb^{++})				
SiO_2 (α quartz)	4.5	37.3	60.2		62.2
fused	3.75	45.2*	64.2		62.2
(assume $\alpha=$	2.2 for Si^{+4})				
		B			
$MgSO_4$	8.2	75.0*	158.5		147.1
$SrSO_4$	11.5	76.6	178.8		129.7
$BaSO_4$	9.32	83.4	184.0	$SO_4^=$	113.4
$PbSO_4$	36.5	78.7	218.0		126.2
Tl_2SO_4	25.5	123.8*	330.0		150.8
Li_2CO_3	4.9	58.1*	98.6		75.2
Na_2CO_3	8.75	70.1*	151.8		111.4
K_2CO_3	4.96	94.5*	161.8		77.2
$MgCO_3$	7.31	44.9	91.4	$CO_3^=$	80.0
$CaCO_3$ (calcite)	8.19	60.9	128.8		93.9
$SrCO_3$	8.85	65.8	143.0		93.9
$BaCO_3$	8.53	76.0	163.0		92.4
$NaNO_3$	6.85	62.3	123.5		103.3
KNO_3	4.37	80.3	127.9		85.6
$AgNO_3$	9.0	64.9	155.6		116.2
$TlNO_3$	16.5	75.3	189.0	NO_3^-	98.9
$Ca(NO_3)_2$	6.54	109.7	213.6		89.4
$Sr(NO_3)_2$	5.33	119.1	211.5		81.2
$Ba(NO_3)_2$	4.95	133.4	227.0		78.2
$Pb(NO_3)_2$	16.8	120.5	304.0		106.1

* Determined from density.

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[9] K. Hojendahl, D. Kgl. Danske Vidensk. Selsk., Math. Fys. Medd. **16**, (2), 59 (1938).

[10] K. Hojendahl, Zeits. f. Physik. Chemie (B), **20**, 54 (1933).

[11] E. Wainer, Trans. Am. Electrochem. Soc. **89**, 47 (1946).

[12] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publications, Inc., New York, 1948), Section I.

dielectric constant of cuprous bromide.[13] In this case, the samples were prepared in the form of disks of compressed powder and the dielectric measurements were corrected for the porosity as determined by comparing the measured density of the disks with the true density of the material. However, the value 4.72 generally quoted for the density of CuBr is incorrect, and it is conceivable that this value may have been used in the porosity calculation. The density determined from x-ray diffraction data is 5.20, and our experimental value for the density of CuBr powder is 5.15. According to our calculations, CuBr might be expected to have a dielectric constant of around 12 instead of 8. Thus, it would seem desirable to remeasure its dielectric constant in order to test this conclusion.

TABLE IV. Temperature coefficients of dielectric constant, polarizability and thermal expansion of dielectric materials.*

Substance	K	$\frac{1}{K}\frac{dK}{dT}$ $(\times 10^{-5})$	$\frac{1}{3V}\frac{dV}{dT}$ $(\times 10^{-5})$	$\frac{1}{\alpha}\frac{d\alpha}{dT}$ $(\times 10^{-5})$
LiF	9.27	37.5	3.5	21.7
NaCl	5.62	34.0	4.0	28.3
KCl	4.68	30.3	3.2	26.9
AgCl	12.3	140.0	3.0	41.0
AgBr	13.1	82.5	3.5	28.3
TlCl	31.9	−40.0	5.1	11.6
TlBr	29.9	−28.0	5.2	12.9
CuCl	10.0	250.0	—	>69.5
CuBr	8.0	160.0	1.9	60.6
$PbCl_2$	33.5	65.5	3.0	14.7
PbI_2	20.8	34.1	3.4	13.5
TiO_2 (rutile)	114.0	−70.0	0.73 0.91	0.36 0.90
$BaTiO_3$ (150°C)	4560.0	−2960.0	0.95	0.90

* *Note:* $1/T = 341\times 10^{-5}$.

In discussing the meaning of the "polarizability" of an ion, it seemed natural to suppose that it might be somewhat less in electrically unbalanced crystals in view of saturation effects attributable to permanent local electrostatic fields. The degree to which this occurs will, of course, depend on the strength of the local field. Some crystals, for example ZnO, very nearly fulfill the requirements of an electrically balanced structure, while others, particularly those containing complex ions such as NO_3^-, etc., include atoms situated in positions where the local static fields are strongly unbalanced.

Dielectric constant, molecular volume and calculated molecular polarizability of a number of crystals having unbalanced Coulomb forces are shown in Tables IIIA and IIIB. The dielectric constants quoted for anisotropic crystals in these tables are obtained by averaging the values corresponding to the three axial directions, if known. In Table IIIA, the polarizability of the molecule is also calculated from the assumed polarizabilities of its ions. The experimental polarizabilities of the titanium compounds in this list are all smaller than the theoretical values, indicating a possible saturation effect. However, the results for anatase and magnesium titanate are well within the tolerance of five percent, showing that the electrostatic unbalance may be small in these materials. No anomalies are observed in the results for silica or the lead compounds.

Table IIIB gives similar results for a number of crystals containing complex ions. The last column shows the polarizability of the complex ion calculated from the experimental data and the previously determined polarizabilities of the metal ions. These results show so much variability that no definite values can be derived for the polarizability of these ions. This might be expected since the oxygen atoms are much more closely bound to the metalloid atom than to the rest of the crystal. Part of the variations observed in Table IIIB may be attributed to inaccuracy of the experimental values for dielectric constant and density since many of these compounds have not been studied as carefully as those listed in Table I.

IV. TEMPERATURE COEFFICIENTS

By differentiating Eq. (6) with respect to temperature, one obtains

$$\frac{1}{\alpha}\frac{d\alpha}{dT}=3\left(\frac{1}{3V}\frac{dV}{dT}\right)+\frac{3K}{(K+2)(K-1)}\cdot\frac{1}{K}\frac{dK}{dT}. \tag{9}$$

This equation expresses the temperature coefficient of the polarizability, $(1/\alpha)(d\alpha/dT)$, in terms of the linear expansion coefficient, $(1/3V)(dV/dT)$, and the T.C. of the dielectric constant, $(1/K)(dK/dT)$. Table IV shows experimental values of temperature coefficients for a number of materials taken from a table compiled by Eucken and Buechner.[13] The T.C. of dielectric constant for TiO_2 is taken from a paper by Bunting, Shelton, and Creamer,[14] while two values are given for the thermal expansion coefficient of the material as obtained by Jonker and van Santen[15] and by von Hippel[16] respec-

TABLE V. Estimated dielectric constants.

Substance	V	K
PbF_2	52.45	31.3
$SrCl_2$	85.75	7.3
K_2O	66.65	6.0
Li_2O	24.64	8.8
Na_2O	42.74	4.65
Rb_2O	76.55	6.2
AgF	29.77	9.1
TlI (cubic)	74.00	26.4
CuF	18.26	92.0
CuI	55.15	15.1
AgI (cubic)	67.80	9.1
$KMgF_3$	64.0	7.5

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[13] A. Eucken and E. Buechner, Zeits. f. Physik. Chemie (B) **27**, 321 (1934).

[14] Bunting, Shelton and Creamer, J. Research Nat. Bur. of Stand. **38**, 337 (1947).

[15] J. H. van Santen and G. H. Jonker, Nature **159**, 333 (1947).

[16] A. von Hippel *et al.*, Ind. Eng. Chem. **38**, 1097 (1946).

tively. We measured the dielectric constant and its temperature coefficient of very pure sintered discs of barium titanate and made the appropriate correction for porosity.[17] The linear expansion coefficient of barium titanate was measured by Jonker and van Santen.[15] The last column in the table gives the T.C. of polarizability calculated from Eq. (9).

Some materials in Table IV have negative temperature coefficients of dielectric constant, although none of these has a negative T.C. of polarizability. Also the T.C. of polarizability is much smaller than that of the dielectric constant, especially when the latter T.C. is large to begin with. In the case of barium titanate, the T.C. of dielectric constant is more than 3000 times that of the polarizability, a fact which indicates that the polarizability is relatively much more nearly invariant. The temperature coefficients of polarizability of the titanium compounds do not vanish as reported by Jonker and van Santen,[15] yet the importance of thermal expansion in causing the large negative temperature coefficients of dielectric constant is correctly interpreted. A Curie-Weiss law can be derived from Eq. (9) which accurately describes the experimental results over a wide range of temperature if one assumes the thermal expansion and the T.C. of polarizability to be constant (linear).

V. DISCUSSION

The polarizabilities of molecules in symmetric types of ionic crystals as calculated by the Clausius-Mosotti equation have been shown to obey the rule of additivity to a very good approximation. This result implies the validity of the Lorentz value of the internal field, which is used in deriving the Clausius-Mosotti equation. Such a conclusion appears to be in contradiction to generally accepted theory.[4] In the particular case of alkali-halides, smaller values of internal field have been thought to be requisite in order to explain the experimentally observed frequencies of resonance in the infra-red range.[9] This subject will be discussed further in a forthcoming paper in which it is intended to show that the Lorentz value of internal field is reasonably consistent with all the experimental data, including the infra-red resonances.

In the case of cubic barium titanate, there is less theoretical justification for the Lorentz value of internal field. However, it may be worth while to point out some errors that have occurred in attempts to calculate the internal field of this material by making inappropriate use of the equations of ferromagnetism.

Mason and Matthias[18] have presented a theory of the dielectric behavior of barium titanate in which the total polarization is comprised of two parts:

$$P=P_e+P_d. \tag{10}$$

The first component, P_e, includes all polarization except that due to titanium dipoles. The second part P_d is that due to the dipoles caused by displacement of the titanium nuclei. For small field strengths and at temperatures above 130°C, where there is no spontaneous polarization, both components are proportional to the local field and P_d is inversely proportional to absolute temperature. Thus the polarizability may be expressed in the following form:

$$\alpha=\alpha_0+\alpha_1(\theta/T), \tag{11}$$

where α_0 and α_1 are parameters having the dimensions of polarizability and θ is the Curie temperature.

The internal field is expressed in a fashion similar to Eq. (5) in which the second component, calculated by Lorentz, is multiplied by an arbitrary factor γ.

$$F_i=E+\gamma P/3\epsilon_0. \tag{12}$$

The dielectric constant may then be calculated in a manner similar to Eq. (7):

$$K=1+\frac{3\alpha}{3V-\alpha\gamma}. \tag{13}$$

The experimental data fit a modified Curie-Weiss law,

$$K=K_0+C/(T-\theta), \tag{14}$$

where C is the Curie constant and θ is the Curie temperature. We find $C=154{,}000$°C and $\theta=118$°C (391°K).

Mason and Matthias have calculated γ from the following relation (in our notation),

$$\gamma=3\theta/C. \tag{15}$$

If one substitutes this expression for γ in Eq. (13) and solves Eqs. (13) and (14) for α, one obtains:

$$\alpha=V\frac{C+(K_0-1)(T-\theta)}{T+(\theta/C)(K_0-1)(T-\theta)}. \tag{16}$$

The experimental result[19] is that $|K_0-1|<10$, therefore:

$$\frac{C}{\theta}=\frac{154{,}000}{391}=393\gg|K_0-1|.$$

Then, especially at temperatures close to the Curie point:

$$\alpha\simeq VC/T. \tag{17}$$

This result is in contradiction with the original assumption (Eq. (10)) that a significant fraction of the total polarization is temperature independent. If this assumption is reasonable, then the internal field constant is not correctly given by Eq. (15). A further objection to the treatment by Mason and Matthias is that it does not take adequate account of thermal expansion.

The same authors have also calculated an internal field constant from the specific heat anomaly, making

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[17] D. F. Rushman and M. A. Strivens, Proc. Phys. Soc. (London) **59**, 1011 (1947).

[18] W. P. Mason and B. T. Matthias, Phys. Rev. **74**, 1622 (1948).

[19] S. Roberts, Phys. Rev. **75**, 989 (1949).

use of the equation:

$$\Delta Q=\frac{\gamma P_0^2}{6\epsilon_0},\quad \text{or}\quad \gamma=\frac{6\epsilon_0\Delta Q}{P_0^2},\tag{18}$$

where ΔQ is the energy required to release the spontaneous polarization P_0. This appears as an anomalous increase in the specific heat over a small range of temperature near the Curie point.

The correct formula is derived from an expression of the change in the total energy density of the system.

$$dU=TdS+EdD,\tag{19}$$

where S is the entropy.

The calculation of the difference in specific heats at constant electric displacement σ_D and at constant electric field σ_E from Eq. (19) is parallel to the corresponding calculation by Becker[20] of the analogous magnetic problem.

$$\sigma_D-\sigma_E=T(\partial E/\partial T)_D(\partial D/\partial T)_E.\tag{20}$$

The first derivative in Eq. (20) may be evaluated from the experimentally determined relation[7] between T, D and E, valid at temperatures above the Curie point.

$$E=[(T-\theta)/\epsilon_0 C]D+\beta D^3.\tag{21}$$

If this equation may be extrapolated below the Curie point and β may be considered constant,

$$\left(\frac{\partial E}{\partial T}\right)_D=\frac{D}{\epsilon_0 C}\tag{22}$$

and

$$\sigma_D-\sigma_E=\frac{T}{2\epsilon_0 C}\left(\frac{\partial D^2}{\partial T}\right)_E.\tag{23}$$

By integrating over a small range of temperature through the Curie point ($\Delta T \ll \theta$) and holding the field $E=0$, one obtains:

$$\Delta Q=\int(\sigma_D-\sigma_E)dT=\frac{\theta P_0^2}{2\epsilon_0 C}.\tag{24}$$

This is the result one would get by substituting Eq. (15) in Eq. (18). Therefore, since these equations are not independent, it is not surprising that they both give approximately the same value for γ, although neither result can be trusted as evidence that γ is different from one. A similar argument with similar shortcomings was presented in an earlier paper by Blattner and Merz,[21] however, their experimental values seem to be more precise and differ by a factor of three from the results of Mason and Matthias.

Following Jonker and van Santen,[15] we prefer the interpretation that the anomalous variations in dielectric constant of cubic barium titanate depend primarily on thermal expansion of the material,

$$V=V_0[1+3\delta(T-T_0)]\tag{25A}$$

with a simultaneous slight variation of polarizability with temperature.

$$\alpha=\alpha_0[1+\phi(T-T_0)],\tag{25B}$$

where V_0 and α_0 are the volume and polarizability at a specified temperature T_0; and δ and ϕ are the corresponding temperature coefficients.

By introducing Eqs. (25A) and (25B) in (7), and expressing the result in the form of (14) and by choosing $T_0=\theta$, one obtains

$$C=\frac{3}{3\delta-\phi};\quad K_0=\frac{3\delta+2\phi}{3\delta-\phi}.\tag{26}$$

The experimental results indicate that both δ and ϕ are positive, as previously considered and indicated in Table IV. Thus, instead of being inversely proportional to temperature, the polarizability is viewed to be remarkably constant, increasing only slightly.

What is perhaps even more significant is, for example, that the value of α_i for the titanium ion is the same in different compounds and that the principle of additive polarizabilities seems to be generally applicable for a wide variety of substances. This principle can be used to advantage in predicting the approximate dielectric constant of new compounds and of compounds for which dielectric data are not available. A list of dielectric constants of such compounds estimated in this way is shown in Table V. Some of these dielectric constants, particularly those of the alkali oxides would be extremely difficult to measure directly owing to the great chemical activity of these compounds. It should be held in mind that the accuracy of these predicted dielectric constants is not too great if one recognizes an uncertainty of five percent in the values of polarizability.

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[20] R. Becker, Theorie der Elektrizitat, II, Elektronentheorie, 6 Ed. (B. G. Teubner, 1933), p. 172.

[21] H. Blattner and W. Merz, Helv. Phys. Acta 21, 210 (1948).