

Temperature Dependence of Dielectric Constants of Cubic Ionic Compounds

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The temperature and pressure dependence of the dielectric constant of a number of cubic halides and oxides with a broad range of dielectric constants have been determined. For low- ϵ compounds the dielectric constant increases with increasing temperature, whereas for high- ϵ compounds the dielectric constant decreases with increasing temperature. Hydrostatic pressure lowers the value of the dielectric constant for all compounds measured. For ferroelectrics and antiferroelectrics a relation has been found between the Curie temperature and the Curie constant. Three effects contribute to the temperature dependence of a dielectric constant: the decrease in the number of polarizable particles per unit volume as the temperature increases, which is a direct result of the volume expansion (A), the increase of the macroscopic polarizability due to the volume expansion (B), and the temperature dependence of the macroscopic polarizability at constant volume (C). The experimental data have been used to calculate these different contributions. It is found that the volume-dependent contribution ($A+B$) is always positive and that the direct temperature contribution (C) can be either positive or negative. Where optical data were available in literature they were used to calculate the contributions of the optical and infrared parts of the polarizability to the temperature and volume dependence of the polarizability. The results are discussed with the use of a classical ionic model.

I. INTRODUCTION

IN a previous paper¹ it has been shown that three effects contribute to the temperature dependence of the dielectric constant ϵ of a cubic or isotropic material. For such a material the macroscopic Clausius-Mossotti formula holds:

$$\frac{\epsilon-1}{\epsilon+2} = \left(\frac{4\pi}{3}\right) \left(\frac{\alpha_m}{V}\right), \quad (1)$$

where α_m is the polarizability of a macroscopic, small sphere with a volume V . The macroscopic polarizability α_m is proportional to the number of unit cells in the sphere, but it may be a complicated function of the polarizabilities of the particles and the geometry of the lattice of the dielectric.

This macroscopic Clausius-Mossotti formula is applicable to all cubic and isotropic materials (see e.g., Fröhlich²). The molecular Clausius-Mossotti formula on the contrary holds only when all polarizable particles in the structure have cubic environments. In that case, and only then, the macroscopic polarizability α_m is equal to the sum of the polarizabilities of all particles, as the fields due to the dipoles inside the sphere cancel each other. When the molecular environments are not cubic for all ions (which is the case, for example, for the oxygen ions in perovskites) the fields due to the dipoles in the sphere do not cancel each other, which may result in very large internal fields. Then the molecular Clausius-Mossotti formula does not hold, but the macroscopic formula (1) remains valid.

In this macroscopic Clausius-Mossotti formula the long-range influence of the material outside the sphere, due to dipole-dipole interactions, is taken into account in a macroscopic way. Although the polarizability α_m of the sphere is a macroscopic quantity, only short-range

influences affect its magnitude. It can, namely, be shown that the internal fields due to the non-cubic environments make themselves noticeable only over rather short distances. In the perovskite structure, for example, the main contribution to these fields arises from the nearest neighbours and a summation of the contributions of dipoles within a sphere having a radius of two or three lattice periods reproduces already within a few percent the exact field factors that are given by Slater.³ Differentiation of formula (1) with respect to temperature at constant pressure gives:

$$\begin{aligned} \frac{1}{(\epsilon-1)(\epsilon+2)} \left(\frac{\partial \epsilon}{\partial T}\right)_p &= -\frac{1}{3V} \left(\frac{\partial V}{\partial T}\right)_p + \frac{V}{\alpha_m} \left(\frac{\partial \alpha_m}{\partial V}\right)_T \\ &\times \frac{1}{3V} \left(\frac{\partial V}{\partial T}\right)_p + \frac{1}{3\alpha_m} \left(\frac{\partial \alpha_m}{\partial T}\right)_V = A+B+C. \quad (2) \end{aligned}$$

The physical processes described by the terms A , B , and C are:

- A : The decrease in the number of polarizable particles per unit volume as the temperature increases, the direct effect of the volume expansion.
- B : An increase of the polarizability of a constant number of particles with the increase of available volume as the temperature increases.
- C : A dependence of polarizability on temperature, the volume remaining constant.

The sum of A and B , which describes the total effect of volume expansion, can be written as:

$$\begin{aligned} A+B &= \frac{1}{(\epsilon-1)(\epsilon+2)} \left(\frac{\partial \epsilon}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \\ &= \frac{1}{(\epsilon-1)(\epsilon+2)} \left(\frac{\partial \epsilon}{\partial p}\right)_T \frac{(1/V)(\partial V/\partial T)_p}{(1/V)(\partial V/\partial p)_T}. \quad (3) \end{aligned}$$

¹ E. E. Havinga, *J. Phys. Chem. Solids* **18**, 253 (1961).

² H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, 1958), 2nd ed., Appendix A3; Sec. 18 and Appendix B2.

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

This equation can be derived by differentiating the Clausius-Mossotti formula (1) with respect to volume at constant temperature. From Eqs. (2) and (3) it follows that A , B , and C can be determined separately by measuring the dielectric constant ϵ , its temperature dependence $(\partial\epsilon/\partial T)_p$ and its pressure dependence $(\partial\epsilon/\partial p)_T$, the thermal expansion coefficient $(1/V) \times (\partial V/\partial T)_p$ and the compressibility $-(1/V)(\partial V/\partial p)_T$.

Apart from the indicated indirect determination of C as the difference between $(A+B+C)$ and $(A+B)$, in principle a direct determination is possible by measuring the temperature dependence of the dielectric constant at constant volume. Differentiation of formula (1) with respect to temperature at constant volume namely gives:

$$C = \frac{1}{(\epsilon-1)(\epsilon+2)} \left(\frac{\partial\epsilon}{\partial T} \right)_V. \quad (4)$$

This method, however, involves experimental difficulties.

The properties of cubic materials with a high dielectric constant suggest that the use of A , B , and C provides indeed a natural way to describe the influence of temperature and pressure on the dielectric constant. For high values of ϵ equation (2) can be approximated by

$$(1/\epsilon^2)(\partial\epsilon/\partial T)_p = A+B+C. \quad (5)$$

On the other hand, a Curie-Weiss law holds for such materials:

$$\epsilon = c/(T - T_c), \quad (6)$$

where c is the Curie constant and T_c the extrapolated Curie temperature. From this equation it follows that

$$(1/\epsilon^2)(\partial\epsilon/\partial T)_p = -1/c. \quad (7)$$

Thus, it is seen that $A+B+C = -c^{-1}$ is in a good approximation constant in a large temperature region, whereas the temperature coefficient $(1/\epsilon)(\partial\epsilon/\partial T)_p$ is strongly temperature dependent. Moreover, for high- ϵ materials the quantity $(1/\epsilon^2)(\partial\epsilon/\partial p)_T$, which is proportional to the sum $(A+B)$, is also more nearly constant with respect to pressure variation than $(1/\epsilon)(\partial\epsilon/\partial p)_T$, the normal pressure coefficient.

In the case of ionic crystals the polarizability α_m of the macroscopic sphere can be separated into two parts (compare reference 2):

$$\alpha_m = \alpha_m^{\text{op}} + \alpha_m^{\text{ir}}. \quad (8)$$

Here α_m^{op} is the optical polarizability due to the motion of electrons relative to the ionic nuclei, and α_m^{ir} is the infrared polarizability, which includes not only the effect of displacements of ions but also that of displacements of electrons thereby induced. The optical polarizability is connected with the optical dielectric constant $\epsilon^{\text{op}} = n^2$ by a macroscopic Clausius-Mossotti formula:

$$(\epsilon^{\text{op}} - 1)/(\epsilon^{\text{op}} + 2) = (4\pi/3)(\alpha_m^{\text{op}}/V). \quad (9)$$

The infrared polarizability α_m^{ir} is obtained as the difference between the static polarizability α_m and the optical polarizability α_m^{op} . The contributions of α_m^{op} and α_m^{ir} to the terms B and C in Eq. (2) can simply be derived by substituting Eq. (8):

$$B = (\alpha_m^{\text{op}}/\alpha_m)B^{\text{op}} + (\alpha_m^{\text{ir}}/\alpha_m)B^{\text{ir}}, \quad (10)$$

$$C = (\alpha_m^{\text{op}}/\alpha_m)C^{\text{op}} + (\alpha_m^{\text{ir}}/\alpha_m)C^{\text{ir}}. \quad (11)$$

B^{op} , C^{op} and B^{ir} , C^{ir} are obtained by replacing α_m in B and C by α_m^{op} and α_m^{ir} , respectively. B^{op} and C^{op} can be determined by measuring the temperature and pressure dependence of ϵ^{op} in an analogous way as B and C by measuring the temperature and pressure dependence of ϵ . The terms B^{ir} and C^{ir} then can be calculated from Eqs. (10) and (11).

As pertinent experimental data are available only for very few compounds, we have determined the values of A , B , and C for a number of halides and oxides with a broad range of dielectric constants, in order to obtain more insight about the factors contributing to the temperature dependence of a dielectric constant. In the discussion of the results optical data reported in literature are also taken into account.

II. EXPERIMENTAL

Measurements have been made partly on single crystals and partly on ceramics (see Table I). In the latter case a correction was applied for the fractional porosity P using the formula $\epsilon = \epsilon_{\text{measured}}(1 + 1.5P)$. This is the small-porosity limit of a relation derived by Wiener⁴ for a continuous dielectric containing vacuum spherical pores. Experiments with SrTiO₃ showed that only for very dense ceramics ($P < 0.05$) results could be obtained that agree with those on single crystals. Therefore the firing and milling conditions of the ceramics were adjusted until such dense materials were obtained. Special care was taken to avoid even small amounts of a second phase. Only samples with a low and temperature-independent loss tangent were used ($\tan\delta < 2 \times 10^{-5}\epsilon$). According to Gevers⁵ such a constant $\tan\delta$ would involve only a negligible positive contribution to the temperature dependence of the dielectric constant [contribution to $(A+B+C) < 0.1 \times 10^{-5}$].

The samples for capacity measurements were prepared in the form of parallel plate condensers, with an area of about 1 cm² and a thickness of 0.5–1 mm. Silver electrodes were painted on the samples, but in a few cases also gold evaporated electrodes were used, which made no difference. The relative change in capacity of a sample with temperature or pressure is equal to the relative change in dielectric constant provided that a correction is made for the change in geometry of the sample.

High capacities were measured with the use of a

⁴ O. Wiener, Leipzig. Ber. **61**, 113 (1909); and **62**, 256 (1910).

⁵ M. Gevers, Philips Res. Repts. **1**, 197, 297 (1946).

TABLE I. The dielectric constant ϵ at 25°C and its temperature and pressure dependence for a number of cubic ionic compounds. Single crystals are marked with an asterisk.

Compound	ϵ	10 ⁵	10 ⁷	Compound	ϵ	10 ⁵	10 ⁷
		$(\epsilon-1)(\epsilon+2)$	$(\epsilon-1)(\epsilon+2)$			$(\epsilon-1)(\epsilon+2)$	$(\epsilon-1)(\epsilon+2)$
		$\times \left(\frac{\partial \epsilon}{\partial T} \right)_p$	$\times \left(\frac{\partial \epsilon}{\partial p} \right)_T$			$\times \left(\frac{\partial \epsilon}{\partial T} \right)_p$	$\times \left(\frac{\partial \epsilon}{\partial p} \right)_T$
		(°K) ⁻¹	(bar ⁻¹)			(°K) ⁻¹	(bar ⁻¹)
NaCl-structure				Perovskite			
KCl*	4.68	5.6	-18.5	BaSnO ₃	18	-0.20	-1.35
KBr*	4.75	5.9	-18.0				
NaCl*	5.62	5.2	-14.5	BaZr _{1-x} Ti _x O ₃			
LiF* ^a	9.27	3.7	-4.5	<i>x</i> =0	39	-0.65	-1.1
MgO*	9.8	1.05	-1.8	0.10	55	-1.25	-1.20
				0.20	92	-1.80	-1.15
CsCl-structure				0.30	150	-1.75	
TlBr*	30	-1.00	-5.9	0.40	245	-1.55	-0.60
				0.50	520	-1.25	
Pyrochlore				0.60	940	-1.15	-0.40
(La _{1-x} Cd _x) ₂ (Zr _{1-x} Nb _x) ₂ O ₇				0.70	3350	-1.05	
<i>x</i> =0.10	26	-0.05	-0.80	Sr _{1-x} Ba _x Sn _{1-x} Ti _x O ₃			
0.20	31	-0.35	-0.70	<i>x</i> =0.40	74	-1.75	
0.40	43	-0.70	-0.65	0.50	130	-1.80	
0.50	54	-0.80	-0.85	0.60	205	-1.80	
0.60	64	-1.00	-0.80	0.70	390	-1.35	
0.70	88	-1.10		0.80	830	-1.20	
0.75	110	-1.10		0.90	4600	-0.95	
0.80	130	-1.15	-0.65				
0.90	210	-1.15		Sr _{1-x} Ba _x TiO ₃			
1.00	650	-1.10	-0.40	<i>x</i> =0*	290	-1.20	-0.80
				0	280	-1.20	-0.90
				0.20	370	-1.20	
				0.40	720	-1.15	
				0.60	2200	-1.10	-0.60
				0.80 ^b	2150	-0.95	
				1.00* ^c	2450	-0.70	-0.26

^a See reference 9.

^b At 50°C.

^c At 150°C; see reference 10.

Schering bridge (Rohde and Schwarz, Type VKB BN 3520), low capacities with a bridge specially designed to determine very small differences (sensitivity about 0.003 pF). The frequency chosen was 250 kc/sec.

The temperature dependence of the dielectric constant was generally determined in the temperature region 20°–150°C. The Curie constants of ferroelectric substances, however, were determined in a temperature region of at least 100°C just above their Curie points, that varied from -240 to 340°C. The dependence of ϵ on hydrostatic pressure was measured at room temperature in a pressure interval 1–5000 kg/cm². In order to minimize the influence of the surrounding oil on the measured capacity change in these pressure experiments, use was made of an electrical screening system. In the most unfavorable case, MgO, the correction due to the variation of the dielectric constant of the oil with the pressure was about 25%. This correction decreases with increasing values of compressibility and/or dielectric constant, and could be neglected in most cases. The accuracy of the measurements was such, that for the halides the pressure dependence of the compressibility had to be taken into account.

Values of the thermal expansion coefficients were taken from literature.⁶ For compounds, where such data were not available, the expansion coefficient was determined from x-ray diagrams at different temperatures. The values of the compressibilities for the halides and MgO were taken from literature,⁷ and the values for SrTiO₃ and BaTiO₃ at 150°C were calculated from elastic constant data.⁸ In the absence of facilities for measuring compressibilities, the values for the other compounds were estimated with the use of the Grüneisen relation

$$\frac{(1/V)(\partial V/\partial T)_p}{(1/V)(\partial V/\partial p)_T} = \frac{\gamma C_v}{V},$$

where γ is the Grüneisen constant, C_v the molar specific

⁶ Alkali halides: W. A. Weyl, Technical Reports Nos. 64, 65, and 66, Pennsylvania State University, Office of Naval Research, 1955 (unpublished). TlBr: M. E. Straumanis and A. Ievens, *Z. anorg. u. allgem. Chem.* **238**, 175 (1938). MgO: S. Ganesan, *Phil. Mag.* **7**, 197 (1962). BaTiO₃: H. F. Kay, *Acta Cryst.* **1**, 229 (1948).

⁷ F. Birch, Geological Society of America, Special papers No. 86, Handbook of Physical Constants (1942).

⁸ E. Poindexter and A. A. Giardini, *Phys. Rev.* **110**, 1069 (1958); D. Berlincourt and H. Jaffe, *ibid.* **111**, 143 (1958).

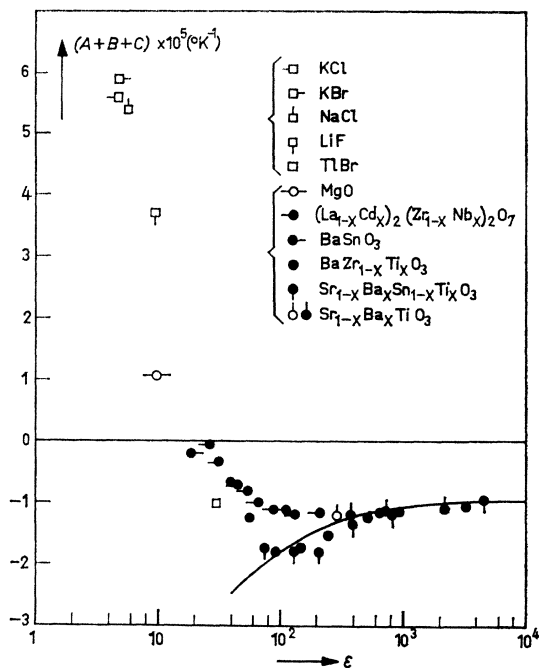


FIG. 1. The temperature dependence of the dielectric constant, $A+B+C=[1/(\epsilon-1)(\epsilon+2)](\partial\epsilon/\partial T)_p$, as a function of ϵ for a number of cubic compounds at room temperature. Open symbols mark single crystals; full symbols, ceramics.

heat at constant volume, and V the molar volume. For C_v the Dulong and Petit value $3R$ was assumed, and for γ the value 1.4 was used, obtained by applying the relation to BaTiO_3 and SrTiO_3 .

III. RESULTS

The experimental results of the determination of the temperature and pressure dependence of the room temperature dielectric constant ϵ of cubic halides and oxides are given in Table I.^{9,10} In order to facilitate a

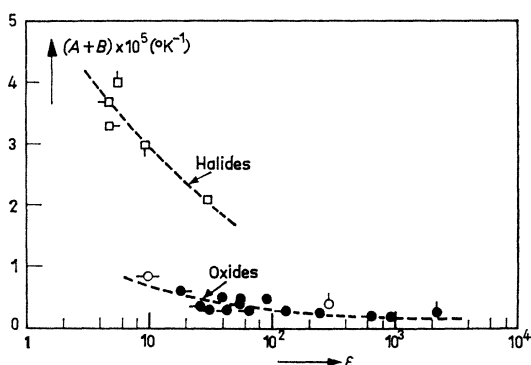


FIG. 2. The volume-dependent part of the temperature dependence of the dielectric constant, $A+B=[1/(\epsilon-1)(\epsilon+2)](\partial\epsilon/\partial T)_p \times (\partial V/\partial T)_p$, as a function of ϵ for a number of cubic compounds at room temperature. The symbols are explained in Fig. 1.

⁹ S. Mayburg, Phys. Rev. **79**, 375 (1950).

¹⁰ J. Klimowski and J. Pietrzak, Acta Phys. Polon. **19**, 369 (1961).

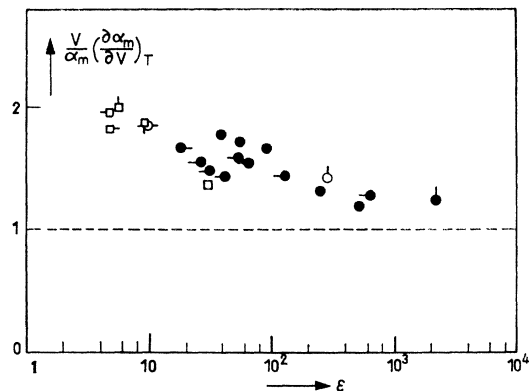


FIG. 3. The relative volume dependence of the macroscopic polarizability, $(V/\alpha_m)(\partial\alpha_m/\partial V)_T$, as a function of ϵ , for a number of cubic compounds at room temperature. The symbols are explained in Fig. 1.

comparison between the compounds we have plotted in Figs. 1–4 the different contributions, calculated from these measurements, as a function of ϵ (logarithmic scale).

Values of the total temperature dependence ($A+B+C$) are shown in Fig. 1. For low values of the dielectric constant ($A+B+C$) is positive, for high values it is negative, the sign reversal being at about $\epsilon=20$. In Fig. 2 values of the total volume-dependent part ($A+B$) are given. Clearly two groups can be distinguished: halides with a large and oxides with a much smaller volume-dependent part. However, this difference is wholly due to a difference in the thermal expansion coefficient $(1/V)(\partial V/\partial T)_p = -3.1$. This is illustrated by Fig. 3 where $(V/\alpha_m)(\partial\alpha_m/\partial V)_T = -B/A$ is plotted as a function of ϵ . Here a steady decrease with increasing ϵ is seen, but no significant difference between halides and oxides is found.

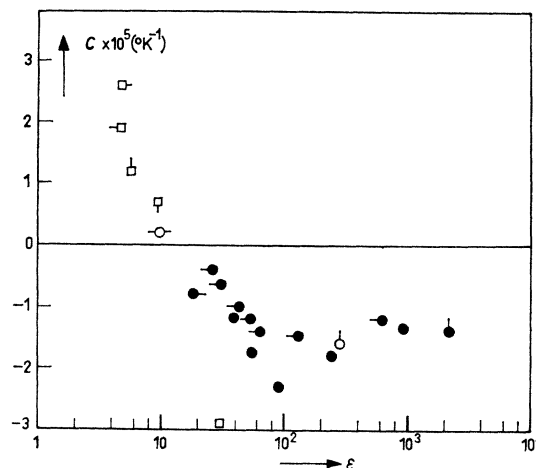


FIG. 4. The temperature dependence of the dielectric constant at constant volume, $C=[1/(\epsilon-1)(\epsilon+2)](\partial\epsilon/\partial T)_V$, as a function of ϵ for a number of cubic compounds at room temperature. The symbols are explained in Fig. 1.

TABLE II. Comparison of some experimental results with literature data.

ϵ	$\frac{1}{\epsilon} \left(\frac{\partial \epsilon}{\partial T} \right)_p \times 10^5$ ($^{\circ}\text{K}^{-1}$)		$\frac{1}{\epsilon} \left(\frac{\partial \epsilon}{\partial p} \right)_T \times 10^5$ (bar^{-1})			$C \times 10^6$ ($^{\circ}\text{K}^{-1}$)			
	This work	Lit. (a)	This work	Lit. (b)	Lit. (c)	This work	Calc. from lit. (b)	(c)	
KCl	4.68	29.6	30.3	-0.96	-1.05	-0.99	1.9	1.6	1.7
KBr	4.75	31.4	...	-0.96	-1.17	-1.30	2.6	2.0	1.5
NaCl	5.62	32.4	34.0	-0.90	-0.98	-0.96	1.2	1.1	1.2
MgO	9.8	10.9	12.7	-0.19	-0.32	-0.15	0.2	-0.3	0.5

^a See reference 11.

^b See reference 9.

^c See reference 12.

Values of the direct temperature effect C are plotted in Fig. 4. For compounds with $\epsilon > 10$ the C term is negative, but for compounds with $\epsilon < 10$ positive values occur. It may be remarked that in the latter case the accuracy of the values of C is rather low because they are obtained as a difference between two large terms $(A+B+C)$ and $(A+B)$. Except for LiF all values given in Figs. 1, 2, 3, and 4 are based on our own measurements of the temperature and pressure dependence of the dielectric constant. Though literature data^{9,11,12} are available for the other alkali halides in these figures and also for MgO, we have repeated the measurements in order to make sure that the C term is indeed positive for these low- ϵ compounds. A comparison between our results and the literature data is given in Table II.

In Fig. 1 room temperature values of $(A+B+C)$ for the different cubic compounds are plotted versus the dielectric constant at room temperature. Consequently, data measured in the cubic high temperature phase of ferroelectrics and antiferroelectrics with a Curie temperature above room temperature are not included. In Fig. 5, therefore, another reference has been chosen: values of $(A+B+C)$ are plotted versus the extrapolated Curie temperatures. A striking result is obtained: For the compounds measured (literature data included¹³⁻¹⁵) there exists an approximately linear relationship between the extrapolated Curie temperature and the reciprocal value of the Curie constant $c^{-1} = -(A+B+C)$. With the assumption that for each compound $(A+B+C)$ is strictly independent of temperature, the straight line in Fig. 5 leads to a relation between the $(A+B+C)$ values of the different compounds and their room-temperature values of ϵ , calculated with the use of the Curie-Weiss law [Eq. (6)]. This is indicated by the full line in Fig. 1. For $\epsilon < 240$,

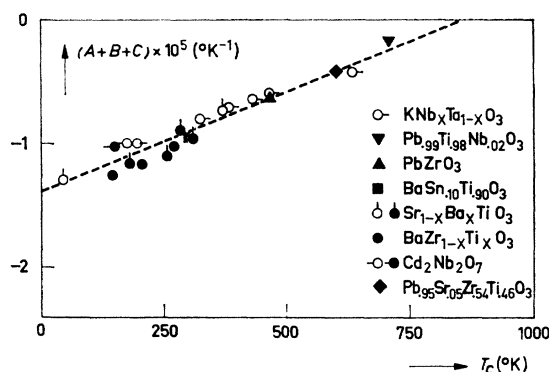


FIG. 5. $(A+B+C)$, the reciprocal Curie constant with reversed sign as a function of the corresponding Curie temperature for (pseudo) cubic ferroelectrics and antiferroelectrics. Open symbols mark single crystals; full symbols, ceramics. Values for $\text{KNb}_x\text{Ta}_{1-x}\text{O}_3$, $\text{Pb}_{0.99}\text{Ti}_{0.99}\text{Nb}_{0.02}\text{O}_3$, and PbZrO_3 and $\text{Cd}_2\text{Nb}_2\text{O}_7$ (single crystal only) are taken from references 13, 14, and 15, respectively. Other data are from our own measurements.

where large deviations occur, this line corresponds with an extrapolation to negative Curie points of the straight line in Fig. 5.

IV. DISCUSSION

1. Combination with Optical Data

The dependence of the index of refraction on temperature and on density is known only for a few compounds. The temperature dependence of their optical dielectric constant $\epsilon^{\text{op}} = n^2$, and its three contributions A , B^{op} ,

TABLE III. Index of refraction n , its dependence on temperature^a and density^b, and the three contributions A , B^{op} , and C^{op} to the temperature dependence of n^2 .

	n	$\left(\frac{\partial n}{\partial T} \right)_p \times 10^6$ ($^{\circ}\text{K}^{-1}$)	$\rho \left(\frac{\partial n}{\partial \rho} \right)_T$	$A \times 10^6$ ($^{\circ}\text{K}^{-1}$)	$B^{\text{op}} \times 10^6$ ($^{\circ}\text{K}^{-1}$)	$C^{\text{op}} \times 10^6$ ($^{\circ}\text{K}^{-1}$)
KCl	1.49	-36	0.23	-3.8	2.3	-0.6
KBr	1.56	-40	0.35	-4.0	2.0	0
NaCl	1.54	-37	0.24	-4.0	2.5	-0.4
LiF	1.39	-13	0.1	-3.4	2.6	-0.2
MgO	1.74	+16	-0.4	-1.0	1.4	0.1

^a See reference 16.

^b See reference 17.

¹¹ $(1/\epsilon)(\partial\epsilon/\partial T)_p$ halides: A. Eucken and A. Büchner, *Z. Physik Chem.* **B27**, 321 (1934). $(1/\epsilon)(\partial\epsilon/\partial T)_p$ MgO: *Table of Dielectric Materials* (Massachusetts Institute of Technology, Cambridge, Massachusetts, 1957), Vol. 5.

¹² G. J. Hill, *Nature* **4822**, 1275 (1962).

¹³ S. Triebwasser, *Phys. Rev.* **114**, 63 (1959).

¹⁴ E. C. Subbarao, *J. Am. Ceram. Soc.*, **43**, 119 (1960).

¹⁵ G. Shirane, F. Jona, and R. Pepinsky, *Proc. Inst. Radio Engrs.* **43**, 1738 (1955).

TABLE IV. The relative contributions of the optical and the infrared part to the polarizability and their influence on the terms B and C .

	ϵ	α_m^{op}/α_m	α_m^{ir}/α_m	$A \times 10^5$ ($^{\circ}\text{K}$) $^{-1}$	$B \times 10^5 = \left(\frac{\alpha_m^{op}}{\alpha_m} B^{op} + \frac{\alpha_m^{ir}}{\alpha_m} B^{ir} \right) \times 10^5$ ($^{\circ}\text{K}$) $^{-1}$	$C \times 10^5 = \left(\frac{\alpha_m^{op}}{\alpha_m} C^{op} + \frac{\alpha_m^{ir}}{\alpha_m} C^{ir} \right) \times 10^5$ ($^{\circ}\text{K}$) $^{-1}$
KCl	4.68	0.50	0.50	-3.8	$7.5 = 1.1 + 6.4$	$1.9 = -0.3 + 2.2$
KBr	4.75	0.55	0.45	-4.0	$7.3 = 1.1 + 6.2$	$2.6 = 0 + 2.6$
NaCl	5.62	0.49	0.51	-4.0	$8.0 = 1.2 + 6.8$	$1.2 = -0.2 + 1.4$
LiF	9.27	0.31	0.69	-3.4	$6.5 = 0.8 + 5.7$	$0.6 = -0.1 + 0.7$
MgO	9.8	0.52	0.48	-1.0	$1.9 = 0.7 + 1.2$	$0.1 = 0.0^5 + 0.0^5$

and C^{op} , calculated with the use of these data,^{16,17} are given in Table III. Comparison with the values of A , B , and C for the static dielectric constants (see Table IV) shows that, while the A term is, of course, equal in both cases, the value of B^{op} (optical) is smaller than that of B (static). So the relative increase in polarizability upon volume enlargement is smaller for the optical polarizability than for the total polarizability α_m . For the alkali halides the increase in optical polarizability with volume cannot even compensate the effect of the decrease in number of polarizable particles per unit volume.

The direct temperature effect C^{op} is small, not only with respect to the absolute values of A and B^{op} , but even in comparison with the resulting term $(A+B^{op})$, which is smaller than each individual term. The total volume-dependent effect $(A+B^{op})$ is thus the main factor contributing to the temperature dependence of the optical dielectric constant of these compounds.

With the use of Eqs. (10) and (11) the terms B and C can be separated into contributions of the optical part α_m^{op} and of the infrared part α_m^{ir} of the polarizability α_m (see Table IV). Here a difference between the alkali halides and MgO is clearly observed. For all compounds the magnitudes of (α_m^{op}/α_m) and (α_m^{ir}/α_m) are comparable, but in the case of the alkali halides the contributions of the optical part α_m^{op} to B and C are almost negligible. For MgO the contributions of α_m^{op} to B and C are of the same order as those of α_m^{ir} .

2. Volume-Dependent Terms

From Table I it is clear that the pressure coefficient is negative for all (cubic ionic) compounds measured: decreasing the volume by increasing the hydrostatic pressure always results in a lower value of ϵ . This means that the volume-dependent contribution $(A+B)$ to the temperature dependence of a static dielectric constant is always positive (Fig. 2): though the number of polarizable particles per unit volume decreases upon volume enlargement, this effect is overcompensated by the increase in polarizability.

According to a thermodynamic relation analogous

¹⁶ R. S. Krishnan, *Progress in Crystal Physics* (Interscience Publishers, New York, 1958), Vol. I, p. 153.

¹⁷ E. Burnstein and P. L. Smith, *Phys. Rev.* **74**, 229 (1948).

to the Maxwell relations, the negative pressure coefficient of the dielectric constant is connected with a positive volume-electrostriction constant¹⁸:

$$(1/V)[\partial V/\partial(E^2)]_{T,p} = -(1/8\pi)(\partial\epsilon/\partial p)_{T,E}. \quad (12)$$

Application of a static electrical field E on a substance, therefore, increases its volume, and it is in this respect analogous to the application of a mechanical stress. The observed positive spontaneous volume-electrostriction at the transition points of ferroelectrics from their cubic phase to a polar phase¹⁹ gives further support for this result.

The volume-dependent effect, defined in Eq. (2), can be written as:

$$A+B = \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_p \left[-1 + \frac{V}{\alpha_m} \left(\frac{\partial \alpha_m}{\partial V} \right)_T \right]. \quad (13)$$

It is seen from Fig. 3 that $(V/\alpha_m)(\partial\alpha_m/\partial V)_T$ has a tendency to decrease with increasing values of ϵ to values only slightly larger than 1. From the lowering of the extrapolated Curie temperature of ferroelectrics when the volume is decreased by hydrostatic pressure (see, e.g., Richard²⁰) it follows that even in the limit $\epsilon \rightarrow \infty$ the term $(V/\alpha_m)(\partial\alpha_m/\partial V)_T$ remains larger than 1. For the measured alkali halides the volume dependence of the infrared part of the polarizability is the main factor contributing to $(V/\alpha_m)(\partial\alpha_m/\partial V)_T$, whereas for MgO the contribution of the optical part of the polarizability is also important. For the other compounds the optical data are unfortunately not available.

In general, α_m will be a rather complicated function of the polarizabilities of the ions. Only for crystals with all ions in a cubic environment, such as the alkali halides, TlBr and MgO, the macroscopic polarizability α_m of a macroscopic sphere can be replaced by $N\alpha_p$, where N is the number of ion pairs in the sphere and α_p is the polarizability of each ion pair. Moreover, the electronic contributions to the infrared part of the polarizability are in this case only due to short-range forces between the ions and therefore proportional to

¹⁸ E. A. Guggenheim, *Thermodynamics* (North Holland Publishing Company, Amsterdam, 1950), 2nd ed., p. 364.

¹⁹ T. W. Forsbergh Jr., in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 17, p. 336.

²⁰ M. Richard, *Ann. Phys. (N. Y.)* **8**, 333 (1961).

their cause, the displacements of the ions. Thus, to a good approximation, the following relation will hold:

$$\alpha_m^{\text{ir}} = \beta N \alpha_p^{\text{ionic}}, \quad (14)$$

α_p^{ionic} being the ionic polarizability per ion pair and β a proportionality constant of the order of unity. If, further, β is assumed to be independent of volume, we have:

$$(V/\alpha_m^{\text{ir}})(\partial\alpha_m^{\text{ir}}/\partial V)_T = (V/\alpha_p^{\text{ionic}})(\partial\alpha_p^{\text{ionic}}/\partial V)_T. \quad (15)$$

The values of $(V/\alpha_p^{\text{ionic}})(\partial\alpha_p^{\text{ionic}}/\partial V)_T$ can be calculated using the classical ionic model for the compounds in question, whereby the ions are held separated by a Born-repulsion energy $U \propto r^{-n}$. This energy leads to a force constant $\partial^2 U/\partial r^2 \propto r^{-(n+2)}$ for the force opposing a motion of the lattice of the positive ions towards that of the negative ions. The ionic polarizability per ion pair is proportional to the reciprocal of this force constant: $\alpha_p^{\text{ionic}} \propto r^{n+2}$. This gives:

$$(V/\alpha_p^{\text{ionic}})(\partial\alpha_p^{\text{ionic}}/\partial V)_T = (n+2)/3. \quad (16)$$

In Table V values calculated in this way are compared with the "experimental" values of $(V/\alpha_m^{\text{ir}})(\partial\alpha_m^{\text{ir}}/\partial V)_T$, obtained directly from the values of B^{ir} and A in Table IV. The agreement is satisfactory, especially as it is obtained with the use of such a simple model. For TlBr this calculation leads to a value of 4.3 for $(V/\alpha_m^{\text{ir}})(\partial\alpha_m^{\text{ir}}/\partial V)_T$, which is nearly equal to the experimental value of $(V/\alpha_m)(\partial\alpha_m/\partial V)_T$. Here, therefore, the optical polarizability is expected to be only slightly dependent on volume.

For compounds with perovskite and with pyrochlore structure the internal fields differ considerably from the Lorentz fields. Therefore α_m is here not merely the sum of the polarizability of the ions, but a complicated function of them. Moreover the infrared part of the polarizabilities α_m^{ir} now contains not only electronic contributions due to the direct short-range interactions with the displaced ions, but also an appreciable part induced by changes of the internal fields due to these ion displacements. For these structures, therefore, the simple theory given cannot be applied.

For the perovskites Slater³ has given a molecular theory in which the internal fields can be calculated with the use of well-known geometrical field factors if the individual polarizabilities of the ions are known. Triebwasser¹³ has analyzed his measurements of the Curie constants of single crystals of KNbO₃—KTaO₃ in terms of this model. In the next paragraph it will be shown that his result concerning the volume-dependent contribution to the Curie constant is not compatible with a slight generalization of our experimental results. However, Triebwasser's theoretical result is very sensitive as to the choice of the individual ionic and electronic polarizabilities. Where we think it is at present not possible to arrive at a non-arbitrary choice

TABLE V. Comparison of experimental values of the dependence of the infrared polarizability on volume with values calculated with Eqs. (15) and (16).

	$\frac{V}{\alpha_m^{\text{ir}}}\left(\frac{\partial\alpha_m^{\text{ir}}}{\partial V}\right)_T$	
	Exp	Calc
KCl	3.4	3.7
KBr	3.5	3.8
NaCl	3.3	3.3
LiF	2.4	2.7
MgO	2.5	3.0
TlBr	4.4 ^a	4.3

^a Relative volume dependence of the total polarizability α_m .

of these polarizabilities, especially of the ionic polarizabilities, we have not tried to adapt this model to our experimental results.

3. The Direct Temperature Effect

The temperature dependence of polarizability at constant volume is mostly negative, but for low- ϵ compounds also positive values occur. It makes an important contribution, $C = (1/3\alpha_m)(\partial\alpha_m/\partial T)_V$, to the temperature dependence of the dielectric constant (compare Fig. 4 with Fig. 1). For compounds with a high dielectric constant at room temperature the negative value of $(1/\epsilon^2)(\partial\epsilon/\partial T)_p = A + B + C$ is in fact almost wholly due to this direct temperature effect C , the volume-dependent term $(A + B)$ being small ($\approx 0.2 \times 10^{-5}$, see Fig. 2). As this volume-dependent term for BaTiO₃ is also small at 150°C ($A + B = 0.15 \times 10^{-5}$), we expect that at all temperatures the value of $(A + B)$ for high- ϵ compounds will be of this order of magnitude. On the other hand, the values of $c^{-1} = -(A + B + C)$ are larger, in most cases even much larger, than 0.2×10^{-5} (see Fig. 5). Thus the volume-dependent contribution to the Curie constant is relatively small, which means that the Curie constant measured at constant pressure is only slightly larger than the Curie constant measured at constant volume. This statement, based on experimental facts, is in contradiction with a result of the theoretical analysis of Triebwasser¹³ mentioned in the preceding paragraph. Namely, Triebwasser arrives at the conclusion that the volume-dependent contribution and the direct temperature-dependent contribution to the Curie constant both are an order of magnitude larger than their difference. This difference determines the value of the Curie constant, and therefore this model leads to a large difference between the Curie constants measured at constant pressure and at constant volume, respectively.

The origin of the C term is mostly discussed with the use of the picture of an ion moving in a potential well. For a parabolic well the polarizability of such an ion is independent of temperature, but any departure from harmonic restoring forces makes its polarizability

temperature-dependent. If the restoring force constant f is larger at a displaced position of the ion than at the potential minimum, an increase in temperature, which causes the particle to spend more time at the displaced positions of higher energy, will result in an enlargement of the mean value of f . The polarizability α , which is proportional to $1/f$, will therefore decrease and $(1/\alpha) \times (\partial\alpha/\partial T)_V$ will be negative. As the classical ionic model with a Born-repulsion energy leads indeed to a potential well for the ions which has anharmonic terms increasing the restoring force, such a model seems to be adequate to explain the occurrence of negative values of the C term. Even when α_m is not merely the sum of the different polarizabilities, this remains in general valid. The basic assumption of the theory of Devonshire²¹ and Slater³ for BaTiO₃ is in fact the motion of the Ti ion in such a well. However, the relation between Curie temperature T_c and $(A+B+C)$ (see Fig. 5), which is in a good approximation a relation between T_c and C as $(A+B)$ is small, cannot be explained by this theory. Moreover, the use of this model to explain the positive values of C found for the alkali halides and MgO involves difficulties. Although the movement of an ion in a well with anharmonic terms that decrease the restoring forces at larger displacements mathematically leads to the result wanted, the appropriate physical interpretation of the origin of such an anharmonicity is not clear.

From Fig. 4 it is seen that positive values of C have been found only for low- ϵ compounds, all of which have the NaCl structure. Preliminary measurements on pressed disks of CsCl, also having a low dielectric constant ($\epsilon=7.2$), indicate that for this compound, having another structure, the C term is negative. Therefore, possibly the structure type has an influence on the C term. Investigations on this problem are in progress.

V. CONCLUSIONS

Three effects contribute to the temperature dependence of the dielectric constant of a cubic compound: the decrease in the number of polarizable particles per unit volume as the temperature increases, which is a direct result of the volume expansion (A), the increase of the macroscopic polarizability due to the volume expansion

(B), and the temperature dependence of the macroscopic polarizability at constant volume (C). Values of these contributions A , B , and C have been determined for a number of halides and oxides by measuring the temperature and pressure dependence of their dielectric constants. The results obtained are:

(1) The temperature dependence of a dielectric constant, $A+B+C=[1/(\epsilon-1)(\epsilon+2)](\partial\epsilon/\partial T)_p$, is positive for ϵ smaller than about 20 and negative for larger values of ϵ .

(2) The volume-dependent contribution to the temperature dependence of a dielectric constant, $A+B=[1/(\epsilon-1)(\epsilon+2)](\partial\epsilon/\partial V)_T(\partial V/\partial T)_p$, is always positive, as $(\partial\epsilon/\partial p)_T$ has been found to be always negative.

(3) From the fact that $(\partial\epsilon/\partial p)_T$ is negative it also follows that the volume-electrostriction constant is always positive.

(4) Between the $(A+B)$ values of halides and oxides with a low dielectric constant there is a large difference, which is wholly due to the difference in thermal expansion coefficient.

(5) Apart from this difference between halides and oxides there is a general decrease of the values of $(A+B)$ going from compounds with a low to compounds with a high value of ϵ .

(6) The direct temperature effect, $C=[1/(\epsilon-1) \times (\epsilon+2)](\partial\epsilon/\partial T)_V$, is negative for $\epsilon > 10$, but for $\epsilon < 10$ positive values occur.

(7) For the alkali halides the dependence of the macroscopic polarizability on volume and temperature is mainly due to the infrared part of this polarizability.

(8) For ferroelectrics and antiferroelectrics a linear relation has been found between the extrapolated Curie temperature and the reciprocal Curie constant $c^{-1} = -(A+B+C)$.

(9) The Curie constant of a ferroelectric measured at constant pressure is only slightly larger than when measured at constant volume, as the volume-dependent contribution is small.

(10) The volume dependence of the infrared polarizability of the alkali halides and of MgO, calculated using a simple Born-repulsion potential, agrees with the experimental results. This model, however, leads to negative values of the C term, which is in contradiction with the positive values found experimentally.

²¹ A. F. Devonshire, *Phil. Mag.* **40**, 1040 (1949).