

## Dielectric behaviour of anisotropic ionic crystals

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**Abstract.** In the case of cubic ionic crystals Havinga has shown that the temperature variation of dielectric constant could be described in terms of volume and temperature effects. By extending his formalism to anisotropic, ionic crystals it has been shown that unlike in cubic ionic crystals where the volume effect consists of a change in the number per unit volume of the polarizable particles and their polarizability with volume, in the case of anisotropic ionic crystals, in addition to these, a variation in the anisotropy of polarizability due to uneven thermal expansion also has to be taken into account. This method of analysis has been examined by taking rutile as an example.

**Keywords.** Dielectric constant; anisotropic ionic crystal; polarizability; Clausius-Mossotti equation; ferroelectric; rutile.

### 1. Introduction

It has been shown by Havinga (1961) that for isotropic ionic crystals there are three physical effects contributing to the temperature variation of dielectric constant. These are (a) decrease in the number of polarizable particles per unit volume with the increase of temperature, (b) increase in the polarizability of a constant number of particles due to an increase in the available volume with the increase of temperature and (c) variation of polarizability with temperature, the volume remaining constant. (a) and (b) together constitute the volume effect and (c) the pure temperature effect. Determination of the variation of dielectric constant with temperature and pressure enables one to estimate the magnitude of (a), (b) and (c). For a number of cubic ionic crystals, the magnitude of these effects has been calculated (Bosman and Havinga 1962; Samara 1968, 1976).

It was considered desirable to examine if this type of analysis could be extended to anisotropic ionic crystals. It will be shown here that unlike in cubic, ionic crystals, where the volume effect consists of a change in the number per unit volume of polarizable particles and their polarizability with volume, in the case of anisotropic, ionic crystals in addition to these, a variation in the anisotropy of polarizability due to uneven thermal expansion also has to be taken into account. The evaluation of the magnitude of this effect has been suggested. This method of analysis has been examined by taking rutile as an example.

## 2. Theory

It is necessary to derive the macroscopic Clausius-Mossotti equation for discussing the temperature variation of dielectric constant in anisotropic ionic crystals.\* For this purpose we shall follow the procedure adopted by Frohlich (1958). Let an anisotropic ionic crystal in the shape of an ellipsoid be brought into a constant electric field. Ellipsoidal shape is just to allow the field inside the crystal to vary not only in magnitude but also in direction. It is necessary to specify the orientation of the ellipsoid with respect to the crystallographic axes. The principal axes of the ellipsoid could be chosen to coincide with those of crystallographic axes in the case of tetragonal and orthorhombic systems. In the trigonal, hexagonal and monoclinic systems only the unique axis can coincide with that of the ellipsoid. For the triclinic system, none of the axes of the ellipsoid need coincide with those of the crystallographic axes. In the derivation of macroscopic Clausius-Mossotti equation we neglect the origin of local field due to microstructure of the medium. Following Frohlich (1958) we define

$$M_k = P_k V = (\alpha_M)_{km} f_m \quad (1)$$

where  $M_k$  ( $k = 1, 2, 3$ ) is the induced dipole moment along the principal axes of the ellipsoid,  $f_m$  ( $m = 1, 2, 3$ ) is the applied electric field along the crystallographic directions and  $(\alpha_M)_{km}$  is the  $km$  component of the macroscopic polarizability of volume  $V$ . The suffix  $M$  in  $\alpha_M$  merely denotes the macroscopic nature of the polarizability of the ellipsoid. It will be proportional to the number of unit cells in the ellipsoid and a complicated function of the ionic polarizabilities and geometry of the lattice. If  $(\alpha_M)_1$ ,  $(\alpha_M)_2$  and  $(\alpha_M)_3$  are the principal coefficients of the ellipsoid, then clearly for the tetragonal, hexagonal, trigonal and orthorhombic systems,  $(\alpha_M)_{11} = (\alpha_M)_1$ ,  $(\alpha_M)_{22} = (\alpha_M)_2$  and  $(\alpha_M)_{33} = (\alpha_M)_3$ . Further for tetragonal, trigonal and hexagonal systems  $(\alpha_M)_1 = (\alpha_M)_2 \neq (\alpha_M)_3$ ,  $c$  being the unique axis. In the monoclinic system with  $b$  as the unique axis only  $(\alpha_M)_{22} = (\alpha_M)_2$ .  $(\alpha_M)_1$  and  $(\alpha_M)_3$  will be a function of  $(\alpha_M)_{11}$ ,  $(\alpha_M)_{33}$  and  $(\alpha_M)_{13}$ . In the triclinic system where none of the crystallographic axes need coincide with the principal axes of the ellipsoid  $(\alpha_M)_1$ ,  $(\alpha_M)_2$  and  $(\alpha_M)_3$  will be a function of  $(\alpha_M)_{11}$ ,  $(\alpha_M)_{22}$ ,  $(\alpha_M)_{33}$ ,  $(\alpha_M)_{13}$ ,  $(\alpha_M)_{23}$  and  $(\alpha_M)_{21}$  (Nye 1957). The above description of the macroscopic polarizability equally holds good for the dielectric susceptibility of the ellipsoid. The dielectric susceptibility is defined as

$$P_i = \chi_{ij} E_j, \quad (2)$$

\*It may be pointed out here that the microscopic Clausius-Mossotti equation is of the form  $(\epsilon - 1)/(\epsilon + 2) = (4\pi/3) \sum N_i a_i$  where  $\epsilon$  is the dielectric constant and  $N_i$  is the number of ions per unit volume having polarizability  $a_i$ . This equation is valid only when all the ions have the cubic site symmetry. Frohlich (1958) derived the macroscopic Clausius-Mossotti equation for cubic ionic compounds which is valid even though the individual ions may not occupy the cubic site symmetry. This is possible because the internal field due to non-cubic environment make themselves noticeable only over rather short distances. The macroscopic Clausius-Mossotti equation is of the form  $(\epsilon - 1)/(\epsilon + 2) = 4\pi/3 (\alpha_M/V)$  where  $\alpha_M$  is the polarizability of a macroscopic small sphere of volume  $V$ . Havinga (1961) employed this equation to discuss the temperature dependence of dielectric constant of cubic ionic crystals.

where  $P_i$  ( $i = 1, 2, 3$ ) is the induced polarization along the principal axes of the ellipsoid and  $E_j$  ( $j = 1, 2, 3$ ) is the effective field along the crystallographic directions. The principal dielectric constants, however, will be  $\chi_1$ ,  $\chi_2$  and  $\chi_3$ .

In the derivation of macroscopic Clausius-Mossotti equation for anisotropic crystals, we shall always refer to the principal coefficients of susceptibility ( $\chi_j$ ) and the macroscopic polarizability ( $(\alpha_M)_j$ ). The application of the Clausius-Mossotti equation in the case of monoclinic and triclinic systems, where the measured values of the dielectric susceptibilities along the crystallographic directions do not directly yield the principal coefficients will be discussed later.

From the definition of principal coefficients of susceptibility and macroscopic polarizability, we have

$$P_j = \chi_j E_j, \quad (3)$$

$$V \cdot P_j = (\alpha_M)_j f_j \quad (j = 1, 2, 3 \text{ refer to the ellipsoid axes}), \quad (4)$$

where  $f_j$  and  $E_j$  are the applied and the effective fields along the  $j$ th axis of the ellipsoid,  $P_j$  is the induced polarization and  $V$  denotes the volume of the ellipsoid.

The effective field inside the ellipsoid is the resultant of the applied field and the depolarization field, *i.e.*,

$$E_j = f_j - N_j P_j, \quad (5)$$

where  $N_j$  is the depolarization factor along the  $j$ th axis of the ellipsoid. From (3), (4) and (5) we get

$$1 = \chi_j \left[ \frac{V}{(\alpha_M)_j} - N_j \right].$$

Noting that  $\chi_j = (\epsilon_j - 1)/4\pi$ , the above equation reduces to

$$\frac{(\epsilon_j - 1)}{(4\pi + (\epsilon_j - 1) N_j)} = \frac{(\alpha_M)_j}{V}. \quad (6)$$

This is the macroscopic Clausius-Mossotti equation for anisotropic crystals.

For the case of cubic crystals where  $N_1 = N_2 = N_3 = 4\pi/3$  and  $(\alpha_M)_1 = (\alpha_M)_2 = (\alpha_M)_3 = (\alpha_M)$ , this equation reduces to the equation derived by Frohlich. For crystals other than cubic,  $N_1$ ,  $N_2$  and  $N_3$  could be evaluated knowing the length-ratios of the principal axes of the ellipsoid (Osborn 1945).

In particular, if the ellipsoid is an ellipsoid of rotation *i.e.* say an oblate spheroid with  $a = b$ , we have

$$\frac{N_1}{4\pi} = \frac{N_2}{4\pi} = \frac{1}{2(m^2 - 1)} \left\{ m^2(m^2 - 1)^{-1/2} \arcsin \left[ \frac{(m^2 - 1)^{1/2}}{m} \right] - 1 \right\}, \quad (7)$$

$$\frac{N_3}{4\pi} = \frac{m^2}{(m^2 - 1)} \left\{ 1 - \frac{1}{(m^2 - 1)^{1/2}} \arcsin \left[ \frac{(m^2 - 1)^{1/2}}{m} \right] \right\}, \quad (8)$$

where  $m = a/c$ .

It should be noted that in the case of cubic, tetragonal, trigonal, hexagonal and orthorhombic systems,  $\epsilon_j$  in (6) are the same as the dielectric constants measured along the crystallographic directions. In the case of monoclinic system with  $b$  as the unique axis, only  $\epsilon_2$  refers to the dielectric constant measured along the crystallographic  $b$  direction.  $\epsilon_1$  and  $\epsilon_3$  do not refer to the dielectric constants along the crystallographic directions  $a$  and  $c$  but have to be computed after measuring dielectric constants along any three directions in the plane perpendicular to the 2-fold axis. This is the general problem of calculating the principal coefficients from measurements in non-principal directions (Nye 1957). In the case of triclinic system, six measurements of dielectric constant have to be made along six directions to calculate  $\epsilon_1$ ,  $\epsilon_2$  and  $\epsilon_3$ .

### 3. Temperature dependence of dielectric constant in anisotropic crystals

Consider equation (6)

$$\frac{(\epsilon_j - 1)}{(4\pi + (\epsilon_j - 1) N_j)} = \frac{(\alpha_M)_j}{V}$$

Partial differentiation of the above equation with respect to temperature at constant pressure yields

$$\begin{aligned} \frac{4\pi/3}{(\epsilon_j - 1)(4\pi + (\epsilon_j - 1) N_j)} \left( \frac{\partial \epsilon_j}{\partial T} \right)_P &= -\frac{1}{3V} \left( \frac{\partial V}{\partial T} \right)_P \\ &+ \frac{1}{3(\alpha_M)_j} \left( \frac{\partial (\alpha_M)_j}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P + \frac{1}{3} \frac{1}{(\alpha_M)_j} \left( \frac{\partial (\alpha_M)_j}{\partial T} \right)_V \\ &+ \frac{1}{3} \frac{(\epsilon_j - 1) N_j}{(4\pi + (\epsilon_j - 1) N_j)} \frac{1}{N_j} \left( \frac{\partial N_j}{\partial T} \right)_P \\ &= A + B_j + C_j + D_j \frac{(\epsilon_j - 1) N_j}{(4\pi + (\epsilon_j - 1) N_j)} \end{aligned} \quad (9)$$

where  $D_j = \frac{1}{3N_j} \left( \frac{\partial N_j}{\partial T} \right)_P$ .

Thus, unlike in the case of isotropic crystals (Havinga 1961) the term  $D_j$  enters in. The significance of  $A$ ,  $B$  and  $C$  has already been explained, it is now required to examine the significance of  $D_j$ .

Consider the simple case of an oblate spheroid. We have  $N_j = 4\pi F_j(m)$  where  $F_j(m)$  denotes the functions as given by equations (7) and (8).

$$\begin{aligned} D_j &= \frac{1}{3N_j} \left( \frac{\partial N_j}{\partial T} \right)_P \\ &= \frac{1}{3} m (\alpha_a - \alpha_c) \frac{\partial (\ln F_j(m))}{\partial m}, \end{aligned} \quad (10)$$

here  $\alpha_a$  and  $\alpha_c$  represent the thermal expansion coefficients along  $a$  and  $c$  respectively. Thus essentially  $D_j$  arises because of the anisotropy in thermal expansion.

could be positive or negative effect depending on the relative magnitudes of the thermal expansion coefficients along the principal axes as well as the sign of  $F'_j(m)$ .

### Pressure dependence of dielectric constant in anisotropic crystals

Consider equation (6)

$$\frac{(\epsilon_j - 1)}{(4\pi + (\epsilon_j - 1) N_j)} = \frac{(\alpha_M)_j}{V}$$

Differentiating the above equation with respect to pressure at constant temperature,

$$\begin{aligned} \frac{4\pi/3}{(\epsilon_j - 1)(4\pi + (\epsilon_j - 1) N_j)} \left( \frac{\partial \epsilon_j}{\partial P} \right)_T &= - \frac{1}{3V} \left( \frac{\partial V}{\partial P} \right)_T \\ &+ \frac{1}{3(\alpha_M)_j} \left( \frac{\partial (\alpha_M)_j}{\partial P} \right)_T + \frac{(\epsilon_j - 1) N_j}{(4\pi + (\epsilon_j - 1) N_j)} \frac{1}{3N_j} \left( \frac{\partial N_j}{\partial P} \right)_T \end{aligned} \quad (11)$$

Analogous to equation (10) we have

$$\frac{1}{3N_j} \left( \frac{\partial N_j}{\partial P} \right)_T = \frac{1}{3} m (\beta_a - \beta_c) \frac{\partial [\ln F_j(m)]}{\partial m}, \quad (12)$$

where  $\beta_a$  and  $\beta_c$  represent linear compressibility coefficients along  $a$  and  $c$ . From (9), (10) and (12) we get

$$\frac{1}{3N_j} \left( \frac{\partial N_j}{\partial P} \right)_T = D_j \frac{\beta_a - \beta_c}{\alpha_a - \alpha_c}. \quad (13)$$

From (9), (11) and (13) we have

$$\begin{aligned} &\frac{4\pi/3}{(\epsilon_j - 1)(4\pi + (\epsilon_j - 1) N_j)} \left( \frac{\partial \epsilon_j}{\partial P} \right)_T \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \\ &= A + B_j + D_j \frac{(\epsilon_j - 1) N_j}{(4\pi + (\epsilon_j - 1) N_j)} \frac{\beta_a - \beta_c}{\alpha_a - \alpha_c} \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \\ &\quad \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \end{aligned} \quad (14)$$

## 5. Evaluation of A, B, C and D

### 5.1 Evaluation of A

A is nothing but the volume expansion coefficient and this could be determined from thermal expansion data.

### 5.2 Evaluation of D

$D_j$  is defined as

$$\frac{1}{3N_j} \left( \frac{\partial N_j}{\partial T} \right)_P$$

$N_j$  at any temperature and consequently  $D_j$  could be evaluated if  $a, b, c$  the semi axes of ellipsoid, are known.  $a, b, c$  could be chosen proportional to lattice parameters  $a', b', c'$ . (In the case of triclinic and monoclinic systems  $a', b'$ , and  $c'$  refer to the component of the lattice parameters along the ellipsoidal axes).

Thus  $c/a = c'/a'$  and  $b/a = b'/a'$ .

From a knowledge of the variation of the lattice parameters as a function of temperature,  $N_j$  and consequently  $(\partial N_j / \partial T)_P$  could be evaluated (Osborn 1945).

### 5.3 Evaluation of B

It is evident from (14) that a knowledge of  $A, D, (1/V) (\partial V / \partial P)_T, \alpha_a, \alpha_c, \beta_a, \beta_c$  and  $N_j$  combined with the variation of  $\epsilon_j$  as a function of pressure would enable us to determine  $B$ .

### 5.4 Evaluation of C

In principle a direct determination of  $C$  is possible by measuring the temperature dependence of dielectric constant at constant volume  $V$ . This however involves experimental difficulties. Hence it has to be determined indirectly. It is clear from (9) that the values of  $A, D$  and  $B$  together with the variation of  $\epsilon_j$ , as a function of temperature would enable us to determine  $C$ .

Thus the various contributions  $A, B, C$  and  $D$  to the temperature dependence of dielectric constant could be evaluated.

## 6. Dielectric behaviour of rutile

We shall now examine the temperature dependence of dielectric constant of rutile ( $\text{TiO}_2$ ) in the light of the above discussion. Rutile belongs to the space group  $P4_2/mnm$  ( $Z = 2$ ) with  $a = 4.594 \text{ \AA}$  and  $c = 2.958 \text{ \AA}$  (Grant 1959). It has a large value of static dielectric constant, with  $\epsilon_c = 170$  and  $\epsilon_a = 86$  at  $300^\circ\text{K}$  (Parker 1961). From

consideration of the polarizabilities of  $\text{Ti}^{+4}$  and  $\text{O}^{-2}$ , rutile was expected to be a potential ferroelectric (Roberts 1949). However, subsequent measurements of its dielectric constant did not reveal any anomaly in the temperature range 1.6 — 1060°K (Parker 1961). Though an ionic crystal, rutile exhibits a decrease in its dielectric constant along both the directions with the increase of temperature.

As mentioned earlier, in order to evaluate the various contributions to the temperature dependence of dielectric constant, we need to have a knowledge of the linear and volume compressibility, linear and volume expansion coefficients as well as the temperature and pressure dependence of the dielectric constant. For rutile all these data are available in the literature and are summarised in table 1. The various contributions  $A$ ,  $B$ ,  $C$  and  $D$  evaluated from this data are given in table 2.

Table 1. Relevant experimental data on rutile at 300°K.

Physical quantity	Magnitude	Reference
lattice parameters	$c = 2.959 \text{ \AA}$ $a = 4.594 \text{ \AA}$	(Grant 1959)
dielectric constant	$\epsilon_c = 170$ $\epsilon_a = 86$	(Parker 1961)
$\partial \epsilon_c / \partial T_P$ $\partial \epsilon_a / \partial T_P$	$-1.94 \times 10^{-1}$ $-0.81 \times 10^{-1}$	Parker 1961
$1/\epsilon_c (\partial \epsilon_c / \partial P)_T$ $1/\epsilon_a (\partial \epsilon_a / \partial P)_T$	$-10.9 \times 10^{-6} (\text{kg/cm}^2)^{-1}$ $-5.6 \times 10^{-6} (\text{kg/cm}^2)^{-1}$	(Gibbs and Jarman 1962)
$1/c (\partial c / \partial T)_P = \alpha_c$ $1/a (\partial a / \partial T)_P = \alpha_a$ $1/V (\partial V / \partial T)_P$	$9.21 \times 10^{-6} / ^\circ\text{K}$ $7.18 \times 10^{-6} / ^\circ\text{K}$ $23.57 \times 10^{-6} / ^\circ\text{K}$	(Kirby 1967)
$1/c (\partial c / \partial P)_T = \beta_c$ $1/a (\partial a / \partial P)_T = \beta_a$ $1/V (\partial V / \partial P)_T$	$-1.038 \times 10^{-7} (\text{kg/cm}^2)^{-1}$ $-1.871 \times 10^{-7} (\text{kg/cm}^2)^{-1}$ $-4.780 \times 10^{-7} (\text{kg/cm}^2)^{-1}$	(Bridgman 1928)

Table 2. Various contributions to the temperature dependence of dielectric constant in rutile at 300°K.

	Along $c$ axis ( $\times 10^{-6} / ^\circ\text{K}$ )	Along $a$ axis ( $\times 10^{-6} / ^\circ\text{K}$ )
$\frac{4\pi/3}{\epsilon - 1} (4\pi + (\epsilon - 1)N) \left( \frac{\partial \epsilon}{\partial T} \right)_P$	-4.89	-13.20
A	-7.86	-7.86
B	8.19	13.41
C	-6.20	-17.95
$\frac{(\epsilon - 1)N}{(4\pi + (\epsilon - 1)N)} \cdot D$	+0.98	-0.80

It should be noted that  $D$  which arises because of the anisotropy in thermal expansion is positive along  $c$  and negative along  $a$  axes. The total volume effect ( $A + B + D$ ) is, however, positive along both  $a$  and  $c$  axes. The volume effect has been found to be positive in all the cubic ionic compounds examined so far (Bosman and Havinga 1962; Samara 1968, 1971). The term  $C$  which denotes the pure temperature effect is negative in both the directions, but is more along the  $a$  axis.  $C$  has been generally found to be negative for cubic ionic compounds having dielectric constant greater than 10. The origin of  $C$  can be understood by considering the motion of an ion in a potential well. For a parabolic well, the polarizability of an ion is independent of temperature, but any deviation from harmonic restoring forces makes the polarizability temperature dependent. Thus, the fact that  $C$  is more along the  $a$  axis than that along the tetragonal  $c$  axis, shows that in rutile, the anharmonicity for the ions is more along the  $a$  axis. Our approach in explaining the temperature dependence of dielectric constant being macroscopic, the physical origin of anharmonicity and its anisotropy cannot be explained without considering the microscopic structure.

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