

Dielectric Relaxation in Ionic Crystals Due to Vacancy Pairs

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Dielectric dispersion data for NaCl, KCl, and KBr have been interpreted by considering the interaction between (i) the vacancy-pair dipoles and (ii) the effective charge of the vacancy and the polarized ions in its vicinity (Boswarva and Franklin's formulation of defect pairs). It has been found that the number of vacancy pairs required to explain the dispersion data is less by a factor of 3 or more than that evaluated from Debye's model.

INTRODUCTION

CATION-ANION vacancy pairs have been considered by several workers¹⁻³ as the main type of relaxing dipoles to explain the dielectric relaxation data of Sastry *et al.*^{1,2} on several ionic crystals. However, interpretation of these results on the basis of a simple Debye model was found to give a value of dipole concentration about 100 times higher than the expected concentration. In the present paper, an attempt has been made to explain the dielectric relaxation data by considering the effect of additional induced moments due to different types of interaction between vacancy pairs as given by Boswarva and Franklin.⁴

THEORY AND CALCULATIONS

The real and imaginary parts of the dielectric constants ϵ' and ϵ'' as given by Debye are

$$\epsilon' = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/(1 + \omega^2\tau^2) \quad (1)$$

and

$$\epsilon'' = 4\pi(\sigma/\omega) + (\epsilon_s - \epsilon_\infty)\omega\tau/(1 + \omega^2\tau^2), \quad (2)$$

where τ is the relaxation time characterizing the dielectric; ω is the angular frequency; σ is the frequency-independent volume conductivity; ϵ_s is the low-frequency value of the real part of the dielectric constant; ϵ_∞ is the high-frequency value of the real part of the dielectric constant.

The intensity of relaxation is controlled by $(\epsilon_s - \epsilon_\infty)$ which is given by

$$\epsilon_s - \epsilon_\infty = 4\pi n\mu^2/3kT, \quad (3)$$

where n is the number of relaxing dipoles and μ is the dipole moment of these dipoles given by ea (a being the cation-anion separation).

Using Eq. (3) Sastry *et al.* evaluated the number of relaxing dipoles (vacancy pairs). Their results, along

with the numbers obtained from statistical considerations, are given in Table II. It is obvious that the values of Sastry *et al.* are several times higher than the statistical values. This discrepancy may be due to the fact that the dipole moment μ will not merely be equal to ea but is ea plus some additional induced moments. Boswarva and Franklin calculated the additional induced moments in the Onsager approximation by considering the interaction between (i) the vacancy-pair dipoles and (ii) the effective charge of the vacancy and the polarized ions in its vicinity. In the crystals the pair dipole is subject to the applied electric field \mathbf{E} and to additional electric fields from the polarized surroundings. The total electric moment of the dipole in a given orientation is

$$\mathbf{m} = \mathbf{u}_0 + \alpha\mathbf{F}, \quad (4)$$

where \mathbf{u}_0 is the vacuum moment of the pair and \mathbf{F} is the total field acting on the dipole. The vacuum moment of the defect pair plus additional moments induced when it is immersed in an infinite medium of dielectric constant ϵ_∞ gives the actual permanent moment \mathbf{u} . On using the dielectric-continuum theory of Mott and Littleton,⁵ \mathbf{u} is found to be

$$\mathbf{u} = e\mathbf{p}[1 + (M_+' + M_-')/8(h_i^2 + k_i^2 + l_i^2)^{3/2}], \quad (5)$$

where (h_i, k_i, l_i) are the Cartesian coordinates of the anion defect centered on the point midway between the defects in the state i , \mathbf{p} is the vector from the cation- to the anion-defect site, and

$$M_+' = \frac{2\alpha_{+eff}}{\alpha_{+eff} + \alpha_{-eff}} \frac{\epsilon_\infty - 1}{4\pi\epsilon_\infty},$$

$$M_-' = \frac{2\alpha_{-eff}}{\alpha_{+eff} + \alpha_{-eff}} \frac{\epsilon_\infty - 1}{4\pi\epsilon_\infty}.$$

α_{+eff} and α_{-eff} are the effective polarizabilities of the cations and anions. The effective polarizabilities are

¹ P. V. Sastry and T. M. Srinivasan, *Phys. Rev.* **132**, 2445 (1963).

² N. A. Economou and P. V. Sastry, *Phys. Status Solidi* **6**, 135 (1964).

³ N. A. Economou, *Phys. Rev.* **135**, A1020 (1964).

⁴ I. M. Boswarva and A. D. Franklin, *Phil. Mag.* **11**, 335 (1965).

⁵ N. F. Mott and M. J. Littleton, *Trans. Faraday Soc.* **34**, 485 (1938).

given by

$$\alpha_{+eff} = \alpha_+ + \alpha$$

and

$$\alpha_{-eff} = \alpha_- + \alpha,$$

where α_+ and α_- are the ionic polarizabilities of the cations and anions, respectively, and α is the displacement polarizability. α can be calculated from the expression⁶

$$\alpha = e^2/4b(1/\rho^2 - 2/\rho a) \exp\{(r_+ + r_- - a)/\rho\}, \quad (6)$$

where ρ is the Born repulsive parameter, taken to be 0.345 Å, and b is a constant taken to be 0.229×10^{-12} erg.

Following Boswarva and Franklin and using Eqs. (5) and (3), we find that the number of vacancy pairs is given by

$$n = \frac{n_{app}}{f} \times \left[\frac{8\pi n_{app}(ea)^2 + 9\epsilon_\infty kT}{12\pi n_{app}(ea)^2 + 9\epsilon_\infty kT} \right], \quad (7)$$

where n_{app} is the value of the number of vacancy pairs required to fit the data of Sastry *et al.* obtained by using Eq. (3). The function f is given by

$$f = \frac{1}{Z} \sum 4g_i h_i^2 \left[1 + \frac{M_+' + M_-'}{8(h_i^2 + k_i^2 + l_i^2)^{3/2}} \right] \times \left[1 + \frac{(M_+' + M_-') + ((\epsilon_\infty + 2)/3a^3)(\alpha_{+eff} + \alpha_{-eff})}{8(h_i^2 + k_i^2 + l_i^2)^{3/2}} \right] \times \exp(-W_i^0/kT), \quad (8)$$

where $Z = \sum g_i \exp(-W_i^0/kT)$, the quantity W_i^0 being the energy of the vacancy pair in the i th state.

The value of f would come out to be unity if the interactions considered in this paper were neglected. A typical value of f is 2.5, but this varies slightly from substance to substance.

TABLE I. Values of parameters used in the calculations.

Parameter	NaCl	KCl	KBr
a Å ^a	2.81	3.14	3.29
r_+ Å ^a	0.98	1.33	1.33
r_- Å ^a	1.81	1.81	1.96
ϵ_∞ ^a	5.62	4.68	4.78
$\alpha_+ \times 10^{24}$ a	0.18	0.83	0.83
$\alpha_+ \times 10^{24}$ b	0.41	1.33	1.33
$\alpha_- \times 10^{24}$ a	3.66	3.66	4.77
$\alpha_- \times 10^{24}$ b	2.96	2.96	4.60
$\alpha \times 10^{24}$ c	4.27	3.84	7.58

^a N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940).

^b J. R. Tessman, A. H. Kahn, and W. Shockley, *Phys. Rev.* **92**, 890 (1953).

^c Calculated.

⁶ A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer Verlag, Berlin, 1957), Vol. 20, p. 246.

The number of relaxing dipoles calculated from this theory and considering only the ground state ($\frac{1}{2}, 0, 0$) of the vacancy pairs is given in Table II for two values of polarizability (values of Pauling and Tessman *et al.*). The values of the parameters used for calculation are given in Table I.

DISCUSSION

It is obvious from Table II that the number of vacancy pairs calculated by Boswarva and Franklin's formulation as presented here is less than the number calculated from the simple Debye theory. Though this number is reduced appreciably, it is still too large as compared to the statistical value. It is also evident that the two sets of polarizability values have little effect upon the number of vacancy pairs. It has been found that the results do not materially change even if the calculations are extended over higher states. The concentration of the vacancy pairs may reduce further if the displacement of the nearest vacancy neighbors and dispersion forces are also taken into account. However,

TABLE II. Number of vacancy pairs obtained from different approaches.

Substance	T (°K)	$n_{\text{statistical}} \times 10^{18}$ per cc	$n_{\text{app}} \times 10^{20}$ per cc	Pauling's values	$n \times 10^{20}$ per cc (present work) Tessman <i>et al.</i> 's values
NaCl	923	1.18	3.48	1.11	1.11
NaCl	1000	4.38	12.2	3.48	3.54
KCl	923	2.75	3.52	1.38	1.39
KCl	1050	15.42	27.4	8.94	9.02
KBr	923	0.62	1.54	0.51	0.50
KBr	980	1.82	4.33	1.36	1.35

the effect of the dispersion forces is not likely to be large as compared to the strong dipolar forces. It may somewhat be interesting to introduce the effect of Debye-Hückel cloud in this theory. The Debye-Hückel theory as applied to ionic crystals will have to be slightly modified because of restricted lattice sites. It is expected that this will produce measurable effects on equilibrium and nonequilibrium defect properties of crystals.⁷⁻⁹

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⁷ G. Everett, A. W. Lawson, and G. E. Smith, *Phys. Rev.* **123**, 1589 (1961).

⁸ A. W. Lawson, *J. Appl. Phys. Suppl.* **33**, 466 (1962).

⁹ A. R. Allnatt and M. H. Cohen, *J. Chem. Phys.* **40**, 1871 (1964).