

MEASUREMENT OF DIELECTRIC PROPERTIES OF METAL HALIDES

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(Received January 22, 1963)

ABSTRACT. The values of the dielectric constants have been determined experimentally by a method described in an earlier paper. The values of the force constant K have been evaluated and compared with other determinations and have been further utilized to compute cohesive energies, compressibilities and reststrahlen frequencies. For cohesive energies both exponential and inverse power models have been assumed. The agreement with experimental values and also with other determinations is reasonable and the analysis presents a simple and adequate approach.

INTRODUCTION

The study of dielectric properties of any material gives the information about the atomic and molecular structure and also about various properties such as compressibilities, reststrahlen frequencies. Therefore, dielectric constants have been measured as functions of densities and of temperatures in substances of various types : pure substances in gas, liquid or solid form; solutions; mixtures of solid particles with other solid particle and so on. The variation with frequency has also been studied over the whole spectrum from static fields through the radio and infra red frequencies to the optical region.

In the present paper we have measured the dielectric constants of alkali halide crystals at radio frequency (15.6MC/S) using the method of mixtures. Experimental technique was based on the method of Hartshorn and Ward (1936) used earlier for vegetable oils by Sharma (1960).

Wiener (1910) has developed a formula taking into account the geometrical shape of the particles and their influence on the distribution of electric field, because the dielectric constant of crystalline powder depends also on the size and shape of the particles. Fricke (1924) has modified Wiener's formula and this modified formula has been used by us.

Since compressibility and reststrahlen frequency of a crystal are related to the dielectric constant and therefore they can be evaluated theoretically. Further, the force constant can also be evaluated with its help and if the law of interaction is known, the interaction energies can also be computed. Dielectric constant data obtained experimentally has been treated for these properties.

T H E O R Y

Wiener (1910) derived an equation for calculating the dielectric constant of mixtures by introducing a constant which depends on the geometrical shape of the particles. He realized that in a continuous medium the geometrical shape of the dispersed particles might influence the distribution of the electric field and consequently the dielectric constant of the mixture. He derived the following formula for calculating the dielectric constant of a mixture :

$$\frac{\epsilon_m - 1}{\epsilon_m + u} = v_1 \frac{\epsilon_1 - 1}{\epsilon_1 + u} + v_2 \frac{\epsilon_2 - 1}{\epsilon_2 + u} \quad \dots (1)$$

where ϵ_m , ϵ_1 and ϵ_2 are the dielectric constants of the mixture and the two components respectively, v_1 , v_2 are the volume ratios of the two components to that of the whole mixture ($v_1 + v_2 = 1$), and u is a constant depending on the shape of the particles. But it was found that equation (1) will hold only for spheres isotropically arranged in a uniform field.

Fricke (1924) has derived a formula for the case of a mixture when one component is dispersed in the other, the latter medium being continuous and homogeneous. Fricke formula is given by the relation

$$\epsilon_m - \epsilon_2 / \epsilon_m + u\epsilon_2 = v_1(\epsilon_1 - \epsilon_2) / (\epsilon_1 + u\epsilon_2) \quad \dots (2)$$

where u is a factor depending on ϵ_1 , ϵ_2 and the shape of the particles. At radio frequencies ϵ_1 and ϵ_2 are complex quantities and u is also complex. Since u is unknown for crystalline particles, it is difficult to solve equation (2) for ϵ_1 .

To avoid such complications, we have used in the present study crystal powders and binding medium of negligible loss. Liquid paraffin has been used as the binding medium.

D E T E R M I N A T I O N O F T H E V A L U E O F ϵ_1

Fricke's equation for ϵ_1 has been solved for ϵ_1 by the method of Burton and Turnbull (1937) as modified by Pradhan and Gupta (1960). The method consists of plotting $(\epsilon_m - \epsilon_2) / (\epsilon_m + u\epsilon_2)$ against v (volume fraction of crystal powder in mixture) on a log log graph paper for several assumed values of u (near about 2). The tangents of each line were evaluated, and by plotting u against the tangents obtained, a smooth curve was obtained. The value of u corresponding to a line giving the value of the tangent equal to unity was obtained. Now using this value of u , a straight line graph between $(\epsilon_m - \epsilon_2) / (\epsilon_m + u\epsilon_2)$ and v was drawn on a log log graph paper (Fig. 1) and the straight line was interpolated to $v_1 = 0.1$. This value of $(\epsilon_m - \epsilon_2) / (\epsilon_m + u\epsilon_2)$ from the graph for $v_1 = 0.1$ gives the value for $v_1 = 1$ on multiplying by 10.

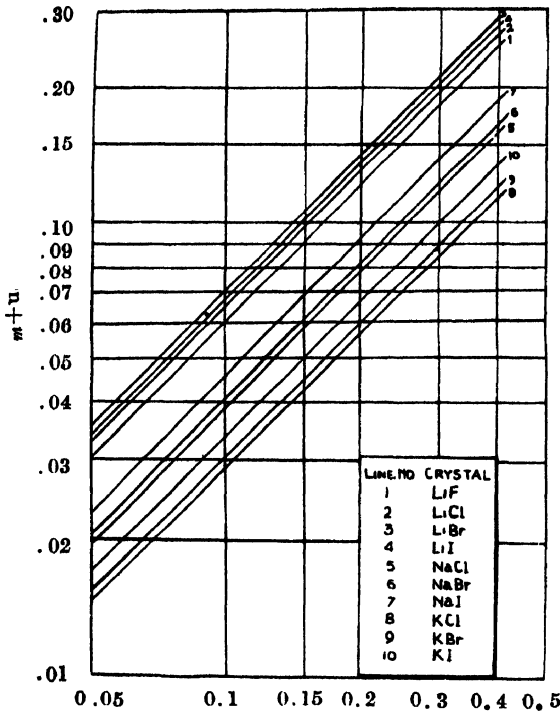


Fig. 1. Fractional volume of particles.

Now at $v_1 = 1$, ϵ_m becomes ϵ_1 and we have

$$\epsilon_m = \frac{1+ux}{1-x} \quad \dots (3)$$

where

$$x = \frac{\epsilon_m - \epsilon_2}{\epsilon_m + u\epsilon_2} \times 10 \quad (\text{for } v_1 = 0.1).$$

MEASUREMENTS AND RESULTS

Hartshorn's method for the measurement of permittivity and power factor of dielectrics at radio frequencies from 10 KC/S to 100 MC/S was employed. The method involves capacitance variation in a tuned circuit, a thermionic voltmeter being employed as a detector of resonance. The basic information for measuring the above parameters has been discussed in detail by Sharma (1960). Since the size and shape of the samples are of utmost importance for obtaining accurate results, mixtures were carefully prepared. The crystal powders were grounded in a mortar and were filtered through a mesh (1000 B.S.). The filtered particles were supposed to be of the same size. These crystal particles were mixed with liquid paraffin in known percentages. The mixtures were stirred well and samples of required size were made. Dielectric constants of mixtures thus measured at

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different concentrations are given in Table I. From this the dielectric constants of alkali halides were evaluated by the method described in the preceding section. They are given in Table III. The constant used for obtaining these dielectric constants are given in Table II.

TABLE I
Dielectric constant of mixtures at radio frequency (15.6MC/S)

Crystal	Concentration of Salt				
	5	10	20	30	40
LiF	2.346	2.500	2.833	3.225	3.677
LiCl	2.355	2.520	2.869	3.316	3.819
LiBr	2.348	2.509	2.864	3.286	3.792
LiI	2.350	2.508	2.861	3.274	3.762
NaCl	2.317	2.435	2.687	2.963	3.260
NaBr	2.318	2.440	2.699	2.984	3.294
NaI	2.326	2.458	2.737	3.049	3.395
KCl	2.294	2.389	2.586	2.797	3.019
KBr	2.295	2.392	2.595	2.812	3.043
KI	2.299	2.398	2.611	2.839	3.085

TABLE II
Values of u and x for alkali halide crystals

Cry- stal	LiF	LiCl	LiBr	LiI	NaCl	NaBr	NaI	KCl	KBr	KI
u	1.12	1.04	0.83	0.91	1.66	1.55	1.41	1.91	1.76	1.60
x	0.60	0.66	0.71	0.68	0.38	0.41	0.46	0.28	0.30	0.33

TABLE III
Dielectric constants of alkali halide crystals at 15.6 MC/S

Crystal	Present work	Pradhan and Gupta (1960)	Born and Huang (1954)	von Hippel (1954)	International Critical Tables (1929)
LiF	9.20	9.27
LiCl	11.00
LiBr	11.92
LiI	11.02
NaCl	5.84	5.86	5.62	5.90	5.90
NaBr	6.04	6.10	5.99
NaI	6.70	6.72	6.60
KCl	4.73	4.77	4.68	5.03
KBr	4.86	4.88	4.78	4.90	5.10
KI	5.07	5.09	4.94	5.40

CORRELATION OF DIELECTRIC CONSTANT WITH
OTHER PROPERTIES

The dielectric properties of ionic crystals are intimately connected with the compressibilities, reststrahlen frequencies and cohesive energies. The ions in the crystal may be regarded as held in their respective positions by (1) the electrostatic forces between the charges carried by them and (2) by forces such as the forces of repulsion, the van der Waals forces and also the homopolar interaction forces if any. In view of the spherical symmetry of the ions, both (1) and (2) types of forces are regarded to be central.

The potential energy $E(r)$ of the crystal per pair of ions can be written as

$$E(r) = -\frac{\alpha e^2}{r} + \phi(r) \quad \dots (4)$$

where α is the Madelung constant. $\phi(r)$ contains all the rest of the energy which is not contained in the electrostatic term $-\frac{\alpha e^2}{r}$.

There are various expressions for $\phi(r)$. Born assumes the form

$$\phi(r) = B e^{-r/\rho} \quad \dots (5)$$

considering only the repulsion interaction between any two neighbouring ions separated by a distance r , whereas the form

$$\phi(r) = Br^{-n} \quad \dots (6)$$

has also been proposed. Equations (5) and (6) do not take into account the van der Waals forces or forces of homopolar character. Usually, the latter forces are not strong enough and can be neglected, but the former, that is the van der Waals forces may be quite important and should be taken into account, as is indicated by an analysis of the available data on dielectric and other properties of crystals by Hardy (1961), Cubicciotti (1959) and Huggins (1937).

Hence the equations (5) and (6) take the form

$$\phi(r) = Be^{-r/\rho} - \frac{C}{r^6} \quad \dots (7)$$

and

$$\phi(r) = Br^{-n} - \frac{C}{r^6}.$$

Equation (8) is known as Lennard-Jones interaction form with empirical values for the index n . Fowler (1955) using $n = 9$, attempts to explain the various properties of crystals, whereas $n = 12$ has been more popular and successful in explaining the data on liquids and gases and in a few cases of solids. For ionic crystals it is found that $n < 12$ is more suitable for lighter salts whereas $n = 12$ is more appropriate for heavier ones as shown by Sharma and Madan (1964). Nevertheless, as has been assumed for liquids and gases, for a unified approach,

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one can reasonably assume $n = 12$ for the data analysis of a number of properties of crystals also. In the present discussion we have considered equation (7) and equation (8) in which $n = 12$.

If the lattice formed by one type of ions is displaced with reference to the lattice of other type of ions by a smaller distance r , then the potential energy of the deformed crystal per pair of ions can be expressed as a power series in r , in which terms involving odd powers of r will be absent as shown by Krishnan and Roy (1951).

The coefficient of r^2 which we denote by ' a ' will determine the reststrahlen frequency of the crystal.

Relation between the force constants used by Born and Huang (1954) and Krishnan and Roy (1951) is given by

$$K = 2 a_1$$

where

$$K = \frac{1}{3} \left[\phi''(r) + \frac{2}{r} \phi'(r) \right]. \quad (9)$$

There is no contribution of the electrostatic interaction to the r^2 term and $\phi(r)$ as given by either equation (7) or (8), as the case may be.

If we consider a uniformly polarized sphere in the absence of an external electric field, the only forces acting are due to the $\phi(r)$ term as shown by Szigeti (1951), the Lorentz effective field F being equal to zero, and we can write a relation connecting K and β the compressibility as

$$K = \frac{3u}{\beta r^2} \quad \dots \quad (10)$$

where u is the volume occupied by an ion pair. Equation (10) for NaCl structure becomes

$$K = \frac{6r}{\beta}. \quad (11)$$

The force constant K , when $F = 0$, is connected with the reststrahlen frequency ω_0 as

$$K = \frac{\epsilon + 2}{\epsilon + 2} m \omega_0^2 \quad (12)$$

where ϵ and ϵ_∞ are the static and high frequency dielectric constants and m is the reduced mass. Krishnan and Roy (1951) treated this problem in a slightly different way. As a result of lattice displacement, there is a development of a homogeneous electric polarization in the crystal and the value of force coefficient, K , instead of being only due to $\phi(r)$ term will be less by an amount proportional to the force due to the polarization field.

From the polarization, the contribution to the force coefficient will be

$$2 a_2 = -\frac{4}{3}\pi N e^2. \quad \dots (13)$$

The total force coefficient will then be

$$2 a = 2 a_1 + 2 a_2 = m \omega_0^2. \quad \dots (14)$$

Therefore,

$$K = 2 a_1 = m \omega_0^2 - 2 a_2. \quad \dots (15)$$

Utilizing the experimentally determined values of the dielectric constant ϵ , we can evaluate the force coefficient K , provided we know the reststrahlen frequency ω_0 . This in turn will enable a determination of the interaction energy of the undeformed crystal as well as its compressibility. The expressions for the interaction energy will depend on whether we are using equation (8) or (7). They are obtained by using relation (9) and are respectively,

$$U_0 = \frac{r_0^2}{44} \left(K - 44 \frac{\alpha e^2}{r_0^3} - 34 \frac{C}{r_0^8} \right), \quad \dots (16)$$

and

$$U_0 = \left(\frac{r_0 \rho^2}{r_0 - 2\rho} \right) \left(3K + 30 \frac{C}{r_0^8} \right) - \left(\frac{\alpha e^2}{r_0} + \frac{C}{r_0^6} \right) \quad \dots (17)$$

The values of β and K (from equations 15 and 12) thus computed are given in Table IV(A) and V respectively, where they have been compared with other determinations as well. The values of U_0 (from equations 16 and 17) are given in Table VI.

TABLE IV(A)

Calculated and experimental values of compressibilities from various Determinations

Crystal	Compressibilities in 10^{-12} Cm ² /dyne.			
	Experimental Cubicciotti (1959)	From equation (11)	Using Equation (15) and ω_0 Experimental	Using Equations (18) and (15)
LiF	1.43	1.53	1.49	1.33
NaCl	3.97	4.16	3.88	4.09
NaBr	4.75	5.48	4.86	4.98
NaI	6.21	7.02	6.50	7.19
KCl	5.50	5.27	5.04	5.08
KBr	6.45	5.39	5.96	6.06
KI	8.07	9.25	7.60	7.85

TABLE IV(B)

Calculated and observed values of reststrahlen frequencies and dielectric constant

Crystal	Reststrahlen Frequency $\times 10^{-13}/\text{Sec.}$					Dielectric Constant	
	Born and Huang (1954)	Krishnan and Roy (1959)	Using β Experimental and Equ. (12)	Using β Experimental and Equ. (11)	Using Equ. (18) and ϵ Experimental	Born and Huang (1954)	Using Equations (11) and (12)
LiF	5.78	5.28	5.92	5.48	6.11	9.20	9.76
NaCl	3.09	2.95	3.16	3.02	2.92	5.84	6.19
NaBr	2.52	2.58	2.71	2.58	2.46	6.04	7.29
NaI	2.20	2.45	2.34	2.30	2.17	6.70	7.84
KCl	2.67	2.51	2.61	2.47	2.65	4.73	4.44
KBr	2.13	2.07	2.11	1.97	2.10	4.86	4.74
KI	1.85	1.89	1.88	1.76	1.80	5.07	5.28

TABLE V

Calculated values of force constants using different crystal properties

Crystal	Force Constant $\times 10^{-4}$				
	From Equ. (12)	From Equ. (15)	From Equ. (11) and Using β Experimental	From Equ. (18)	Krishnan and Roy (1951)
LiF	7.90	8.10	8.45	9.07	8.26
NaCl	4.07	4.36	4.26	4.13	4.22
NaBr	3.27	3.69	3.78	3.60	3.80
NaI	2.77	2.99	3.13	2.95	3.38
KCl	3.58	3.75	3.43	3.72	3.48
KBr	3.74	3.32	3.07	3.27	3.20
KI	2.29	2.79	2.65	2.70	2.90

TABLE VI
Comparison of observed and calculated values of cohesive energies in
K Cal/mole.

Crystal	Experimental Born and Huang (1954)	From Equation (17)			From Equation (16)		
		Using <i>K</i> from Equ.(12)	Using <i>K</i> from Equ.(11)	Using <i>K</i> from Equ.(18)	Using <i>K</i> from Equ.(12)	Using <i>K</i> from Equ.(11)	Using <i>K</i> from Equ.(18)
LiF	239.4	236.0	232.2	280.7	280.0	279.1
NaCl	184.7	185.5	184.4	185.6	199.2	198.6	199.0
NaBr	175.9	177.9	175.1	183.1	188.8	187.4	187.8
NaI	166.3	166.4	164.3	165.5	174.4	173.2	173.8
KCl	167.8	169.3	170.2	168.6	177.8	178.3	177.4
KBr	161.2	159.0	162.9	161.7	167.8	170.2	169.5
KI	152.8	155.2	153.2	152.9	160.1	158.7	158.4

Recently, data have been compiled by Cubicciotti (1959) for the compressibility and hence one could also take these experimental values of β and use them to evaluate *K*. This can then give the reststrahlen frequency using either equation (12) or (15). The values of ω_0 thus computed are given in Table IV(B). Using experimental ω_0 and experimental β , theoretical values of dielectric constant can also be calculated. These values of dielectric constants are given in Table IV(B), where they have been compared with experimental values.

Assuming that there are also local distortions present, Szigeti (1951) obtained an equation relating the reststrahlen frequency and the dielectric constant, which is slightly different from equation (12)

$$(\epsilon - \epsilon_\infty)/(\epsilon_\infty + 2)^2 = 4\pi N(Se)^2/9m\omega_0^2 \quad \dots (18)$$

where *S* is unity for Lorentz approximation. Equation (12) is obeyed better than equation (18) particularly for the lighter salts as shown by Hardy (1961), who has given a detailed discussion of the importance of relations (12) and (18). The effect of equation (18) can be seen if one uses this relation and the experimental ϵ to calculate the energy and the compressibility which can then be compared with the values given in Tables (VI) and IV(A) based on equation (12).

Comparison of various values in Tables IV(A), IV(B), V and VI shows that there is a reasonable agreement between various values among themselves and also with the experimentally determined values.

Cohesive energies calculated on the basis of exponential model are in good agreement with the experimental energies. Inverse power model using $n = 12$ gives comparatively a poor agreement. This is to be expected because this is more suitable for heavier elements. Most of the salts considered here are lighter and $n < 12$ will be more appropriate.

A comparison of various reststrahlen frequencies indicates that the values of ω_0 calculated by using experimental data of compressibilities is in better agreement with the observed frequencies, thus placing confidence in the new values of compressibilities.

ACKNOWLEDGMENT

The authors are grateful to Professor P. N. Sharma for his interest in the investigation.

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