

Electronic Polarizabilities of Ions in Crystals*

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A set of electronic polarizabilities has been obtained from a least-squares fit of experimental refraction data using simple additivity and a Lorentz factor of $4\pi/3$. Except for the fluorides, the electronic polarizability values of the alkali-halide crystals calculated from this set agree with the experimental data within 3 percent. Similar least-squares fits were attempted with various values of the Lorentz factor, the best fit being obtained for $4\pi/3$. On the basis of $4\pi/3$, the additivity assumption and the alkali-halide set, polarizabilities have been obtained for other ions. The best values for the sodium *D* line in A^3 are $Li^+ 0.03$, $Na^+ 0.41$, $K^+ 1.33$, $Rb^+ 1.98$, $Cs^+ 3.34$, $F^- 0.64$, $Cl^- 2.96$, $Br^- 4.16$, $I^- 6.43$, $Ca^{++} 1.1$, $Sr^{++} 1.6$, $Ba^{++} 2.5$, $O^{--} 0.5-3.2$, $S^{--} 4.8-5.9$, $Se^{--} 6.0-7.5$, $Te^{--} 8.3-10.2$, $Ag^+ 2.4$, $Cu^+ 1.6$, $Cu^{++} 0.2$, $Zn^{++} 0.8$, $Cd^{++} 1.8$, $Ge^{4+} 1$, $Sn^{4+} 3.4$, $Pb^{++} 4.9$. Values represented by a spread indicate ions that cannot be treated additively.

I. INTRODUCTION

THE problem of electronic polarizability of individual ions has been the subject of numerous investigations. Among these, determinations of the polarizabilities of gaseous ions have been performed by Pauling¹ from the theory of the quadratic Stark effect, by Born and Heisenberg² from the Rydberg-Ritz correction for spectral series, by Fajans and Joos³ from an examination of the indices of refraction of salts in aqueous solution, and by Mayer and Mayer⁴ from spectral data.

A list of polarizabilities of ions in ionic crystals obtained from recent data, and an examination of the validity of employing the Lorentz factor, may be of use in the study of ferroelectricity. In the present paper we obtain values for the electronic polarizability of the alkali ions and halide ions from an examination of the indices of refraction of the alkali-halide crystals. Using these values as a starting point, we shall then obtain values for the electronic polarizability of a second group of ions that combine with the halide ions and form crystals for which optical data are available. In turn, the polarizabilities of these ions will be used to determine the polarizabilities of other ions which do not form halide crystals.

Throughout, the calculations will be based on the assumptions that the crystals considered are purely ionic, that the electronic polarizability of a crystal is simply the sum of the electronic polarizabilities of the individual ions, and that the Lorentz factor has a normal value of $4\pi/3$. The consistency of the results can be considered as a measure of the validity of these

assumptions. It has been suggested⁵ that the normal Lorentz factor may not be correct for some crystals because of the extended nature of the electronic charge distribution and the consequent overlapping of neighboring ions. However, we shall see that for the alkali-halides, the best fit of the empirical data is achieved with the normal Lorentz factor.

An empirical examination of the additivity of the total polarizability, ionic plus electronic, of individual ions has been made by Roberts.⁶

II. THE LORENTZ FACTOR

At optical frequencies, let the field acting on any ion of a crystal be expressed as

$$E_{\text{eff}} = E + LP, \quad (1)$$

where E is the applied field, P is the electronic polarization or electric dipole moment per unit volume, and L is a constant called the Lorentz factor. E and P are assumed to be in the same direction, and L is the same for all ions. The optical dielectric constant K is defined by

$$KE = E + 4\pi P. \quad (2)$$

The optical dielectric constant and the index of refraction n are related, $K = n^2$.

If the electronic dipole moment p_i induced at each ion is proportional to E_{eff} , the factor of proportionality defines the electronic polarizability, α_i ,

$$p_i = \alpha_i E_{\text{eff}}. \quad (3)$$

For a crystal of diatomic molecules, the dipole moment of each molecule is

$$p_m = p_i + p_j = (\alpha_i + \alpha_j) E_{\text{eff}} = \alpha_m E_{\text{eff}}. \quad (4)$$

Then

$$P = \alpha_m E_{\text{eff}} / V_m, \quad (5)$$

* Part of this work was reported to the American Physical Society at its meeting in Chicago of June 20-22, 1946. See W. Shockley, *Phys. Rev.* **70**, 105 (1946).

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¹ L. Pauling, *Proc. Roy. Soc. (London)* **A114**, 191 (1927).

² M. Born and W. Heisenberg, *Z. Physik* **23**, 388 (1924).

³ K. Fajans and G. Joos, *Z. Physik* **23**, 1 (1924).

⁴ J. E. Mayer and M. G. Mayer, *Phys. Rev.* **43**, 605 (1933).

⁵ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), second edition, p. 16.

⁶ S. Roberts, *Phys. Rev.* **76**, 1215 (1949).

TABLE I. Molecular volume V_m , indices of refraction at various wavelengths n_C, n_D, n_F, n_∞ , and molecular electronic polarizability α_m of the alkali-halides. $C=6563\text{\AA}$, $D=5893\text{\AA}$, $F=4861\text{\AA}$.

Compound	$V_m(\text{\AA}^3)$	n_C	n_D	n_F	n_∞	$\alpha_m(\lambda=D)$	$\alpha_m(\lambda=\infty)$
LiF	16.21		1.3915		1.386 ^b	0.920A ³	0.909A ³
LiCl	33.74		1.662		1.658 ^b	2.980	2.903
LiBr	41.37		1.784		1.778 ^b	4.159	4.138
LiI	54.00		1.955		1.949 ^b	6.248	6.226
NaF	24.65	1.3246	1.3258	1.3285	1.3188	1.186	1.163
NaCl	44.58	1.5407	1.5443	1.5534	1.5252	3.360	3.263
NaBr	52.95	1.6355	1.6412	1.6555	1.6111	4.560	4.388
NaI	67.46		1.7745		1.706 ^b	6.721	6.264
KF	38.07		1.352		1.360 ^b	1.966	2.008
KCl	61.86	1.4872	1.4904	1.4984	1.4770	4.272	4.173
KBr	71.42	1.5547	1.5594	1.5716	1.5332	5.508	5.293
KI	87.68	1.6589	1.6670	1.6876	1.6238	7.790	7.388
RbF	44.85	1.394	1.396	1.399	1.388	2.572	2.572
RbCl	69.93	1.4903	1.4936	1.5016	1.4765	4.856	4.712
RbBr	80.50	1.5483	1.5528	1.5646	1.5283	6.147	5.920
RbI	98.30	1.6397	1.6474	1.6672	1.6061	8.532	8.093
NaCl CsF	54.22	1.476	1.478	1.482	1.469	3.664	3.604
Structure CsCl	86.49	1.531	1.534	1.543	1.516	6.419	6.235
(α) CsBr	94.12 ^a	1.577	1.582	1.594	1.566	7.497	7.329
CsI	112.80 ^a	1.653	1.661	1.681	1.618	9.952	9.435
CsCl CsF	47.18	1.575	1.578	1.583	1.566	3.738	3.674
Structure CsCl	69.43	1.6377	1.6418	1.6523	1.6209	5.984	5.829
(β) CsBr	78.95	1.6924	1.6984	1.7126	1.6676	7.271	7.020
CsI	94.94	1.7784	1.7876	1.8115	1.7378	9.577	9.119

^a Values obtained from density measurements.^b Values taken from Højendahl.

where V_m is the volume of the crystal divided by the number of molecules in the crystal.

From the above equations, it follows simply that

$$\alpha_m = V_m \frac{n^2 - 1}{Ln^2 - L + 4\pi} \quad (6)$$

If L has the normal Lorentz value of $4\pi/3$, then Eq. (6) becomes the familiar Lorentz expression

$$\alpha_m = \frac{3V_m n^2 - 1}{4\pi n^2 + 2} \quad (7)$$

For an assembly of parallel point dipoles, located at the lattice points of a diagonal cubic lattice, such as the NaCl, CsCl, CaF₂, and ZnS type lattices, with equal dipoles at like-ion lattice points, the local field at any lattice point, E_{eff} , is correctly given by Eq. (1) with $L=4\pi/3$. For other lattices, the Lorentz factor L may have different values, but the sum of the three Lorentz factors for three mutually perpendicular arrangements of the parallel point dipoles is always 4π .

III. THE ALKALI-HALIDES AND THE EMPIRICAL DETERMINATION OF THE LORENTZ FACTOR

We shall first consider the alkali-halide crystals. These have either the NaCl-type structure in which the Na ions and Cl ions are each arranged on a f.c.c. lattice and together form a s.c. lattice, or the CsCl type structure in which the Cs ions and Cl ions are each arranged on a s.c. lattice and together form a b.c.c. lattice.

In Table I are listed the molecular volume V_m , the

indices of refraction n at several wavelengths, and the electronic polarizability α_m for the alkali-halide molecules. The molecular volumes are obtained from x-ray data.⁷ The refraction data are obtained from the compilation by Winchell.⁸ The value of n for $\lambda=\infty$ is obtained by extrapolating to $\lambda=\infty$ the straight line which is fitted, by the method of least squares, to the Cauchy relation $n=A+B/\lambda^2$. In those cases where the only refraction data available are for the D line, the values of n for $\lambda=\infty$ are taken from a calculation by Højendahl.⁹ The molecular electronic polarizability α_m is computed from Eq. (7).

On the basis of the values of the molecular electronic polarizability α_m , contained in Table I, a set of electronic polarizabilities α_A and α_H , was computed for all the alkali and halide ions by minimizing the sum of the squares of the differences in electronic polarizability as

TABLE II. Electronic polarizability of alkali ions and halides ions for $\lambda=D$ and $\lambda=\infty$.

	$(\lambda=D)$ $\alpha_A(\text{\AA}^3)$	$(\lambda=\infty)$ $\alpha_A(\text{\AA}^3)$		$(\lambda=D)$ $\alpha_H(\text{\AA}^3)$	$(\lambda=\infty)$ $\alpha_H(\text{\AA}^3)$
Li ⁺	0.029	0.029	F ⁻	0.644	0.759
Na ⁺	0.408	0.255			
K ⁺	1.334	1.201	Cl ⁻	2.960	2.974
Rb ⁺	1.979	1.797	Br ⁻	4.158	4.130
Cs ⁺	3.335	3.137	I ⁻	6.431	6.199

⁷ R. W. G. Wyckoff, *Crystal Structure* (Interscience Publishers, New York, 1951).⁸ A. Winchell, *Microscopic Characters of Artificial Inorganic Substances or Artificial Minerals* (John Wiley and Sons, Inc., New York, 1931) second edition.⁹ K. Højendahl, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **16**, No. 2, 90 (1938).

TABLE III. Comparison of electronic polarizabilities, α_m of the alkali-halides, taken from Table I, with $\alpha_A + \alpha_H$, taken from Table II, (a) for $\lambda = D$; (b) for $\lambda = \infty$. First line α_m . Second line $\alpha_A + \alpha_H$. All values are in Å^3 .

	F	Cl	Br	I
	(a) $\lambda = D$			
Li	0.920	2.980	4.159	6.248
	0.673	2.989	4.187	6.459
Na	1.186	3.360	4.560	6.721
	1.053	3.368	4.566	6.839
K	1.966	4.272	5.508	7.790
	1.981	4.297	5.495	7.767
Rb	2.572	4.856	6.147	8.532
	2.623	4.939	6.137	8.409
Cs	3.664	6.419	7.497	9.952
	3.979	6.295	7.493	9.765
	(b) $\lambda = \infty$			
Li	0.909	2.903	4.137	6.225
	0.788	3.003	4.159	6.228
Na	1.162	3.263	4.387	6.263
	1.014	3.227	4.385	6.452
K	2.007	4.172	5.294	7.388
	1.960	4.175	5.330	7.397
Rb	2.528	4.712	5.920	8.092
	2.556	4.772	5.929	7.996
Cs	3.604	6.235	7.328	9.436
	3.896	6.108	7.266	9.333

given by Table I and as given by $\alpha_A + \alpha_H$. Thus,

$$\sum_i (\alpha_{m_i} - \alpha_{A_i} - \alpha_{H_i})^2 \quad (8)$$

was made a minimum. The summation is over the 20 alkali-halide compounds of Table I. Cs compounds of the NaCl structure only are included in order to deal with crystals all having the same structure.

Table II gives the resulting computed values of electronic polarizability of the alkali and halide ions for $\lambda = 5893\text{Å}$ and $\lambda = \infty$. The electronic polarizability of one of the ions must be selected arbitrarily in order to form such a table, since the minimizing of (8) still permits the polarizability of each of the alkali ions to be raised by a constant amount if the polarizability of each of the halide ions is reduced by the same amount. The electronic polarizability of Li^+ was taken as 0.029Å^3 from Pauling's calculation. Since Li^+ has the smallest electronic polarizability, large percentage errors in its value produce only small percentage changes in the polarizability of the other ions, and of course, no change in the value of $\alpha_A + \alpha_H$.

In Tables III(a) and III(b), the electronic polarizability values α_m are compared with $\alpha_A + \alpha_H$ obtained from Table II for $\lambda = D$ and $\lambda = \infty$. Deviations are no greater than 3 percent except for the fluorides where they are as high as 22 percent for $\lambda = D$ and 13 percent for $\lambda = \infty$.

In order to determine the best empirical value to use for the Lorentz factor, L in Eq. (6), the electronic polarizabilities α_m of Table I were recomputed for $\lambda = \infty$, using Eq. (6) with various values of L . For each value of L , a new set of electronic polarizabilities was computed for the 9 ions of Table II, by minimizing

expression (8). A comparison is made in Fig. 1 between values of the sum of the squares of the deviations $\sum_i (\alpha_{m_i} - \alpha_{A_i} - \alpha_{H_i})^2$ for different values of L , and also between values of the mean square deviation divided by the mean polarizability,

$$\frac{\sum_i (\alpha_{m_i} - \alpha_{A_i} - \alpha_{H_i})^2}{\sum_i \alpha_{m_i}},$$

for different values of L . The second expression is the more significant measure of the effect of varying L , because as L increases, the calculated values of α_{m_i} , α_{A_i} , and α_{H_i} all decrease toward zero, causing $\sum_i (\alpha_{m_i} - \alpha_{A_i} - \alpha_{H_i})^2$ to approach zero.

It can be seen that these expressions have their minima in the neighborhood of $L = 4\pi/3$ and are definitely larger for values of L less than $4\pi/3$. Hence, it may be concluded that the normal Lorentz factor of $4\pi/3$ appears to be highly satisfactory for computing a set of electronic polarizabilities for the individual alkali and halide ions such that the appropriate sums give the electronic polarizabilities of the alkali-halide molecules.

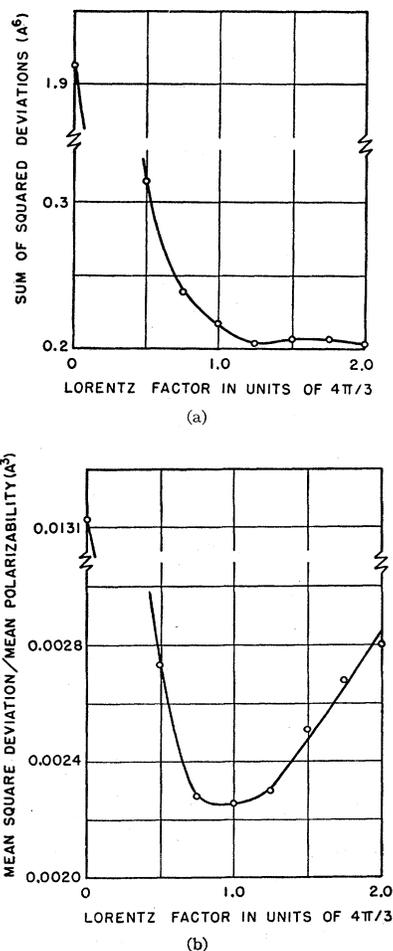


FIG. 1. Plots of the sum of the squared deviations, $\sum_i (\alpha_{m_i} - \alpha_{A_i} - \alpha_{H_i})^2$ vs Lorentz factor; and the mean square deviation/mean polarizability, $\sum_i (\alpha_{m_i} - \alpha_{A_i} - \alpha_{H_i})^2 / \sum_i \alpha_{m_i}$, vs Lorentz factor.

TABLE IV (a). Molecular volumes, indices of refraction, molecular electronic polarizabilities, and electronic polarizabilities for ions which form diagonal cubic halide crystals.

Compound	V_m (A ³)	n_D	α_m (A ³)	Ion	α (A ³) Electronic polarizability	α_{AV} (A ³)
AgCl	42.67	2.071	5.327	Ag ⁺	2.37	
AgBr	47.98	2.252	6.593	Ag ⁺	2.44	2.4
TlCl	56.36	2.247	7.727	Tl ⁺	4.8	
TlBr	62.57	2.418	9.225	Tl ⁺	5.1	5.2
TlI	73.98	2.78	12.238	Tl ⁺	5.8	
CuCl	39.49	1.973	4.628	Cu ⁺	1.67	
CuBr	45.83	2.116	5.872	Cu ⁺	1.71	1.6
CuI	55.16	2.345	7.899	Cu ⁺	1.47	
CdF ₂	39.37	1.56	3.038	Cd ⁺⁺	1.75	
SrF ₂	48.38	1.440	3.043	Sr ⁺⁺	1.76	1.7
SrCl ₂	87.75	1.6499	7.465	Sr ⁺⁺	1.55	
CaF ₂	40.49	1.43385	2.516	Ca ⁺⁺	1.23	See Table IV(b)
BaF ₂	59.21	1.475	3.976	Ba ⁺⁺	2.69	See Table IV(b)
NH ₄ Cl	57.78	1.6426	4.984	NH ₄ ⁺	2.024	
NH ₄ Br	66.28	1.7108	6.187	NH ₄ ⁺	2.029	See Table IV(b)
NH ₄ I	95.03	1.7031	8.796	NH ₄ ⁺	2.365	

IV. OTHER IONS

In Table IV (a), the list of electronic polarizabilities for $\lambda = D$ is extended to other ions that form compounds with the halide ions and for which data are available. It is again assumed that polarizabilities are additive. The crystals of IV (a) are all of the diagonal cubic type. The normal Lorentz factor $L = 4\pi/3$ is used.

In Table IV (b), noncubic crystals are listed. For these the Lorentz factor is not strictly $4\pi/3$. However, only crystals having small optical anisotropy are listed. Therefore, in the absence of more accurate Lorentz

factors for many of the noncubic crystals which we shall examine, we shall continue to use $L = 4\pi/3$ together with the average value of the index of refraction.

In Table V, additional compounds are listed and values calculated for the electronic polarizability of various ions, again assuming additivity, and using the polarizability values already obtained above. Experimental data not available in Winchell⁸ were obtained from the International Critical Tables.¹⁰

As we get further away from the alkali-halides, homopolar binding may be expected to play an increased

TABLE IV (b). Data for ions which form halide crystals which are not diagonal cubic.

Compound	V_m (A ³)	n_D	α_m	Ion	α (A ³) Electronic polarizability	α_{AV} (A ³)
BaCl ₂	85.88	$n_\alpha = 1.73024$ $n_\beta = 1.73611$ $n_\gamma = 1.74196$	8.235	Ba ⁺⁺	2.32	2.5
CaCl ₂	84.26	1.600 1.605 1.613	6.937	Ca ⁺⁺	1.02	1.1
MgF ₂	34.45 ^a	$n_0 = 1.378$ $n_e = 1.390$	1.914	Mg ⁺⁺	0.63	
MgCl ₂	64.34	1.675 1.59	5.581	Mg ⁺⁺	-0.34	
ZnCl ₂	73.01	1.687 1.713	6.705	Zn ⁺⁺	0.79	
FeCl ₂	63.44	$n_0 = 1.567$ $n_0 - n_e$ weak	4.948	Fe ⁺⁺	-0.97	
PbCl ₂	78.96	2.199 2.217 2.260	10.713	Pb ⁺⁺	4.79	
SnI ₄	220.97 ^a	2.106	28.157	Sn ⁴⁺	2.43	
GeBr ₄	207.79 ^a	1.6269	17.578	Ge ⁴⁺	0.95	
SiCl ₄ (liquid)	189.94 ^a	1.412	11.281	Si ⁴⁺	-0.56	
NH ₄ F	46.74 ^a	1.328	2.263	NH ₄ ⁺	1.62	

2.0
See Table IV (a)

^a Values obtained from density measurements.

¹⁰ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1926), first edition.

TABLE V. Polarizabilities of additional ions.

Compound	V_m (A ³)	n_{AV}	α_m (A ³)	Ion	α (A ³)
LiKSO ₄	98.00	1.4721	6.552	SO ₄ ⁻⁻⁻	5.19
Na ₂ SO ₄	87.62	1.477	5.910	SO ₄ ⁻⁻⁻	5.09
K ₂ SO ₄	107.22	1.4952	7.467	SO ₄ ⁻⁻⁻	4.80
Rb ₂ SO ₄	120.23	1.5136	8.634	SO ₄ ⁻⁻⁻	4.68
Cs ₂ SO ₄	138.70	1.5635	10.761	SO ₄ ⁻⁻⁻	4.09
CaSO ₄	75.10	1.587	6.025	SO ₄ ⁻⁻⁻	4.9
SrSO ₄	76.93 ^a	1.626	6.500	SO ₄ ⁻⁻⁻	4.8
BaSO ₄	86.08	1.639	7.393	SO ₄ ⁻⁻⁻	4.9
ZnSO ₄	68.71	1.666	6.099	SO ₄ ⁻⁻⁻	5.3
Tl ₂ SO ₄	125.53	1.8708	13.620	SO ₄ ⁻⁻⁻	3.2
PbSO ₄	81.12	1.884	8.896	SO ₄ ⁻⁻⁻	4.1
(NH ₄) ₂ SO ₄	122.46	1.5256	8.966	SO ₄ ⁻⁻⁻	5.0
NaOH	31.15	1.3576	1.630	OH ⁻	1.22
Li ₂ CO ₃	58.34 ^a	1.522	4.246	CO ₃ ⁻⁻⁻	4.2
Na ₂ CO ₃	70.05 ^a	1.498	4.901	CO ₃ ⁻⁻⁻	4.1
CaCO ₃	76.47 ^a	1.6073	6.306	CO ₃ ⁻⁻⁻	5.2
SrCO ₃	66.17	1.615	5.512	CO ₃ ⁻⁻⁻	3.8
BaCO ₃	73.88	1.627	6.252	CO ₃ ⁻⁻⁻	3.8
ZnCO ₃	46.83	1.751	4.559	CO ₃ ⁻⁻⁻	3.8
PbCO ₃	67.22	1.897	7.447	CO ₃ ⁻⁻⁻	2.7
KNO ₃	80.29	1.4489	5.139	NO ₃ ⁻	3.81
RbNO ₃	78.65 ^a	1.518	5.688	NO ₃ ⁻	3.71
CsNO ₃	87.58 ^a	1.553	6.691	NO ₃ ⁻	3.36
AgNO ₃	64.85	1.753	6.326	NO ₃ ⁻	3.93
Sr(NO ₃) ₂	117.55 ^a	1.567	9.166	NO ₃ ⁻	3.7
Ba(NO ₃) ₂	133.78 ^a	1.572	10.508	NO ₃ ⁻	4.0
PbNO ₃	121.26	1.782	12.167	NO ₃ ⁻	3.69
NaCN	49.54	1.452	3.191	CN ⁻	2.78
KCN	68.97	1.410	4.079	CN ⁻	2.75
Li ₂ O	24.64	1.644	2.129	O ⁻⁻⁻	2.07
Cu ₂ O	39.72 ^a	2.705	6.428	O ⁻⁻⁻	3.2
CaO	27.60	1.837	2.910	O ⁻⁻⁻	1.8
SrO	34.03	1.870	3.690	O ⁻⁻⁻	2.0
BaO	42.12	1.980	4.959	O ⁻⁻⁻	2.5
ZnO	24.18 ^a	2.009	2.903	O ⁻⁻⁻	2.1
CdO	25.77	2.49	3.900	O ⁻⁻⁻	2.2
PbO	39.35	2.622	6.218	O ⁻⁻⁻	1.4
SiO ₂	37.58 ^a	1.5472	2.845	O ⁻⁻⁻	1.7
SnO ₂	35.20	2.0288	4.280	O ⁻⁻⁻	0.9
CaS	45.81	2.137	5.940	S ⁻⁻⁻	4.8
SrS	50.57	2.107	6.447	S ⁻⁻⁻	4.7
BaS	64.01	2.155	8.380	S ⁻⁻⁻	5.9
ZnS	39.63	2.368	5.729	S ⁻⁻⁻	4.9
CdS	49.70 ^a	2.514	7.586	S ⁻⁻⁻	5.8
CaSe	51.61	2.274	7.165	Se ⁻⁻⁻	6.1
SrSe	60.45	2.220	8.181	Se ⁻⁻⁻	6.5
BaSe	72.53	2.268	10.042	Se ⁻⁻⁻	7.5
CaTe	63.86	2.51	10.039	Te ⁻⁻⁻	8.9
SrTe	67.71	2.408	9.945	Te ⁻⁻⁻	8.2
BaTe	85.24	2.440	12.672	Te ⁻⁻⁻	10.2
ZnTe	55.91	3.56	10.618	Te ⁻⁻⁻	9.8
Na ₂ SiO ₃	84.34	1.523	6.149	SiO ₃ ⁻⁻⁻	5.3
CaSiO ₃	66.30	1.628	5.617	SiO ₃ ⁻⁻⁻	4.5
BaSiO ₃	80.45	1.675	7.216	SiO ₃ ⁻⁻⁻	4.7
CuSO ₄	73.46 ^a	1.732	7.013	Cu ⁺⁺	2.3

^a Values obtained from density measurements.

role. The simple additivity assumption of the pure ionic crystal would tend to lose validity. This perhaps may explain the negative polarizability values in Table IV (b) and the spread in polarizability values exhibited in Table V. It would also greatly decrease the usefulness of polarizability values deduced from data involving the presence of the ion in question is only one compound.

Table VI lists the polarizabilities as determined by

Fajans and Joos, Born and Heisenberg, Pauling, and the present method.

V. CONCLUSION

As may have been expected, the assumption of simple additivity in crystals leads in some cases to an appreciable spread of the values of the electronic polarizability of an ion as calculated from different compounds. This would result from a departure from the ideal ionic crystal state and an overlapping and distortion of the ionic wave functions. The values obtained, however, do give an approximate measure of the electronic polarizabilities of various ions in crystals, rather than as "free" ions.

In the case of the alkali-halides, we have seen that departure from additivity is not to be attributed to the departure of the Lorentz factor from its normal value

TABLE VI. Electronic polarizabilities of ions (in A³).

Ion	Fajans and Joos	Born and Heisenberg	Pauling	Present paper ($\lambda = D$)
Li ⁺	0.08	0.075	0.029	0.03
Na ⁺	0.196	0.21	0.179	0.41
K ⁺	0.88	0.87	0.83	1.33
Rb ⁺	1.56	1.81	1.40	1.98
Cs ⁺	2.56	2.79	2.42	3.34
Cu ⁺	1.6
Ag ⁺	2.4
Be ⁺⁺	0.04	...	0.008	...
Mg ⁺⁺	0.12	0.012	0.094	...
Ca ⁺⁺	0.51	...	0.47	1.1
Sr ⁺⁺	0.86	1.42	0.86	1.6
Ba ⁺⁺	1.68	...	1.55	2.5
Zn ⁺⁺	0.8
Cd ⁺⁺	1.8
B ³⁺	0.02	...	0.003	...
Al ³⁺	0.067	0.065	0.052	...
Sc ³⁺	0.35	...	0.286	...
Y ³⁺	0.55	...
La ³⁺	1.3	...	1.04	...
C ⁴⁺	0.012	...	0.0013	...
Si ⁴⁺	0.04	0.043	0.0165	...
Ti ⁴⁺	0.236	...	0.185	...
Ge ⁴⁺	1.
Zr ⁴⁺	0.37	...
Sn ⁴⁺	3.4
Ce ⁴⁺	0.73	...
O ⁻⁻⁻	2.75	...	3.88	0.5-3.2
S ⁻⁻⁻	8.6	...	10.2	4.8-5.9
Se ⁻⁻⁻	11.2	...	10.5	6.0-7.5
Te ⁻⁻⁻	15.7	...	14.0	8.3-10.2
F ⁻	0.98	0.99	1.04	0.64
Cl ⁻	3.53	3.05	3.66	2.96
Br ⁻	4.97	4.17	4.77	4.16
I ⁻	7.55	6.28	7.10	6.43
NH ₄ ⁺	2.0
Tl ⁺	5.2
Fe ⁺⁺	-1.
Cu ⁺⁺	0.2
Pb ⁺⁺	4.9
CN ⁻	2.8
NO ₃ ⁻	3.4-4.0
CO ₃ ⁻⁻⁻	2.7-5.2
SiO ₃ ⁻⁻⁻	4.5-5.3
SO ₄ ⁻⁻⁻	3.0-5.3

TABLE VII. Molecular volumes, cation volumes, volume per O^{--} ion, molecular polarizabilities, cation polarizabilities, and polarizability of O^{--} in the presence of various ions. All values in Å^3 .

Compound	V_m	V_{cation}	$V_{O^{--}}$	$(4\pi/3)\alpha_m$	$(4\pi/3)\alpha_{cation}$	$(4\pi/3)\alpha_{O^{--}}$
BeO	13.8	0.1	13.7	5.4	0.03	5.4
MgO	18.6	1.15	17.4	7.3	0.4	6.9
CaO	27.5	4.05	23.4	11.9	2.0	9.9
SrO	33.2	6.0	27.2	14.4	3.6	10.8
BaO	41.6	10.3	31.3	19.1	6.5	12.6
ZnO	24.0	1.7	22.3	11.3	1.2	10.1
CdO	26.1	3.8	23.3	16.6	4.5	12.1
HgO	32.0	5.5	26.5	20.4	5.2	15.2
Al_2O_3	42.3	0.6	13.6	17.2	0.2	5.6
Li_2O	24.7	0.9	22.8	8.9	0.1	8.7
TiO_2	30.9	1.3	14.7	19.5	0.8	9.3

of $4\pi/3$. On the contrary, the best fit of a set of electronic polarizabilities to the empirical data is obtained for a Lorentz factor of $4\pi/3$.

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APPENDIX I

It has been reported by one of the authors¹¹ that some regularity can be observed in the spread of polariza-

¹¹ W. Shockley, Phys. Rev. **73**, 1273 (1948).

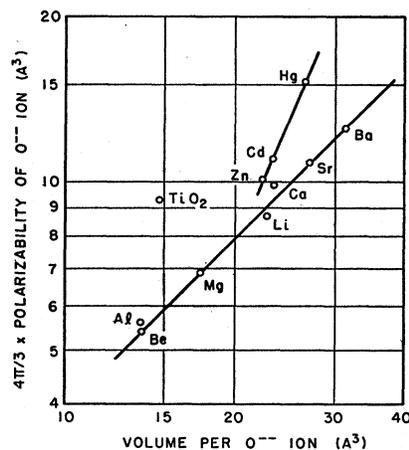


FIG. 2. Polarizability of the O^{--} ion as a function of volume per O^{--} ion for several compounds.

bilities obtained for oxygen. Figure 2 shows a plot of the polarizability of the O^{--} ion as a function of the volume per O^{--} ion. The molecular volumes were determined from density measurements and the cation volumes are those given by empirical ionic radii.⁷ (See Table VII.)

Polarizabilities for O^{--} were obtained from refractive index data, using a Lorentz factor of $4\pi/3$ for all compounds, regardless of high refractive anisotropy. The cation polarizabilities for determining the O^{--} polarizabilities were taken from Pauling's work. The graph of Fig. 2 shows that values of the O^{--} polarizability of Al, Be, Mg, Li, Ca, Sr, and Ba oxides fall near one line; Zn, Cd, and Hg about 20 percent higher and TiO_2 about 80 percent higher.