type II contain considerable quantities of nitrogen. At this stage it is not clear whether this line is due to a local mode, an electronic transition or a two-phonon combination activated by the nitrogen impurities. In this connection it is interesting to note that the combination $\Sigma^{(1)}(0)+\Sigma^{(2)}(0)$ at 2339 cm^{-1} is close to 2333 cm^{-1}; however, the former is Raman-active in $Z'(X'X')Y'$ and $Y'(Z'Z')X'$, Raman-inactive in $Z'(X'Z')Y'$ and $Z'(Y'X')Y'$ and inactive in the infrared, whereas the 2333-cm^{-1} feature appears in all of these (see Table VI). Therefore, $\Sigma^{(1)}(0)+\Sigma^{(2)}(0)$ taken together with a relaxation of the selection rules caused by the nitrogen impurities may account for the feature at 2333 cm^{-1}.

Johnson and Loudon[9] and Bilz *et al.*[10] have discussed the shape and topological features of the critical points in the second-order spectra of silicon, germanium, and diamond. It appears that the experimentally observed features in the second-order Raman spectrum of diamond are not amenable to such analysis. Modulation techniques[43] such as those used in the analogous problems of the critical points in the optical-reflection spectra of semiconductors might be usefully applied to the study of the second-order Raman and infrared spectra.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Professor Peter Fisher and Professor Sergio Rodriguez for stimulating discussions and comments, and to Professor H. J. Yearian who oriented some of the diamond crystals used in this study.

---

[43] B. O. Seraphin and N. Bottka, Phys. Rev. Letters **15**, 104 (1965); G. Ascarelli and A. Barone, Nuovo Cimento **37**, 818 (1965); G. Ascarelli, Phys. Rev. **179**, 797 (1969); G. W. Gobeli and E. O. Kane, Phys. Rev. Letters **15**, 142 (1965); and W. E. Engler, H. Fritzsche, M. Garfinkel, and J. J. Tiemann, *ibid.* **14**, 1069 (1965).

PHYSICAL REVIEW B VOLUME 1, NUMBER 4 15 FEBRUARY 1970

Semiempirical Calculations of Ionic Polarizabilities and van der Waals Potential Coefficients for the Alkaline-Earth Chalcogenides*

I. M. Boswarva†
Metallurgy Department, Imperial College, London, England

(Received 28 July 1969)

Electronic polarizabilities for the ions of the alkaline-earth chalcogenides have been calculated by assuming an additivity law within the family of salts and a Lorentz factor of $\frac{4}{3}\pi$, and using experimental refractive indices and interionic distances. It is shown that the additivity assumption is well obeyed, and the Lorentz factor value of $\frac{4}{3}\pi$ gives the best fit to the data. Each polarizability obtained has been related to a mean excitation or characteristic energy for the ion, and hence the coefficients of the dipole-dipole and dipole-quadrupole terms of the van der Waals interaction energy derived.

1. INTRODUCTION

Two approaches to the evaluation of the polarizabilities of ions in ionic crystals are well established. The first, pioneered by Tessman, Kahn, and Shockley[1] (hereafter referred to as TKS) and recently extended by Pirenne and Kartheuser[2] and Kartheuser and Naylor[3] assumes that within a family of salts the electronic polarizability of each substance is the sum of the electronic polarizabilities of the individual ions and that each ion polarizability is constant within the family. Under the further assumption that the electrostatic interactions between ions are purely of the dipole-dipole type the effective field acting on an ion $E_{\text{eff}}=E+LP$, where E is the externally applied field, P is the electronic polarization and the Lorentz factor, L, has a value of $\frac{4}{3}\pi$. The polarizability per ion pair α_m is then related to the refractive index of the salt, n, through the Clausius-Massotti relation

$$\alpha_m=(3V_m/4\pi)(n^2-1)/(n^2+2)\,, \tag{1}$$

where V_m is the volume occupied by an ion pair. The ion polarizabilities α_i are chosen to attain a best fit to α_m values throughout the family and the achievement of such a fit is taken as a measure of the validity of the assumptions.

All the previous workers have considered the alkali halides, although TKS have derived the only previously reported values of alkaline-earth ion polarizabilities by substracting their halide values from the ion-pair polarizabilities of the alkaline-earth halides. With these alkaline-earth values, a further step to the alkaline-earth chalcogenide family gives chalcogenide values, as does a study of the alkali chalcogenides. Such a process implies the dubious extension of the concept of constancy of an ion polarizability within one family to

---

* Work performed under contract at the National Bureau of Standards, 1967.

† Contribution of the National Bureau of Standards, not subject to copyright.

[1] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

[2] J. Pirenne and K. Kartheuser, Physica **30**, 2005 (1964).

[3] K. Kartheuser and K. A. Naylor, Phys. Letters **19**, 548 (1966).

a constant value in at least two families of salts of different crystal structure. This approach fails to give, for example, a constant O^{2-} ion polarizability in the alkaline-earth oxides implying either the constant ion-polarizability concept in the alkaline-earth chalcogenides is invalid or an ion does not possess the same polarizability in different crystal structures. In their paper, TKS favor the first conclusion but, as the main work of this paper shows, it is possible to achieve remarkably good additivity of ion polarizabilities to account for the ion-pair polarizabilities in the alkaline-earth chalcogenides by working entirely within that family, pointing to the breakdown of constancy of ion polarizabilities across families.

The second approach starts from the relation between the ion polarizability and the optical absorption due to that ion

$$\alpha=\frac{C}{N}\int_0^\infty \frac{\mu(\Delta E)}{(\Delta E)^2}d(\Delta E), \tag{2}$$

where $\mu(\Delta E)$ is the absorption coefficient per unit energy increment ΔE, N is the number of ions per unit volume, and C is a material-independent constant. As the absorption due to the cation and the anion in an ionic solid are in widely separated regions of the spectrum this approach should give polarizabilities directly without the assumptions needed in the first approach. Unfortunately, the absorption spectra required lie in the far ultraviolet and are not available for most materials. Lynch[4] has successfully used the method on the data of Philipp and Ehrenreich[5] for KCl, KBr, and KI to obtain ionic polarizabilities and less satisfactorily Hajj[6] has used the approach for all the alkali halides with the limited spectra of Eby, Teegarden, and Dutton.[7] However, some use may be made of Eq. (2) if it is assumed that the bulk of the absorption due to a particular ion occurs near some characteristic energy $\bar{E}$, so that the equation reduces to

$$\alpha=e^2h^2n/4\pi^2m\bar{E}^2, \tag{3}$$

where n is the effective number of electrons in the ion, e is the electronic charge, m is the electron mass, and h is Planck's constant. Ruffa[8,9] has considered how the characteristic energy of a free ion is changed when the ion is placed in the crystalline environment and so obtains crystal ion polarizabilities from Pauling's[10] free-ion values derived from the quadratic Stark effect. This paper employs Eq. (3) in the opposite way, that is, to find the characteristic energies of ions from the polarizabilities previously determined and so use the following relations (Mayer[11]):

$$c_{ij}=3\bar{E}_i\bar{E}_j\alpha_i\alpha_j/2(\bar{E}_i+\bar{E}_j), \tag{4}$$

$$d_{ij}=\frac{27\alpha_i\alpha_j\bar{E}_i\bar{E}_j}{8e^2(\bar{E}_i+\bar{E}_j)}\left(\frac{\alpha_i\bar{E}_i}{n_i}+\frac{\alpha_j\bar{E}_j}{n_j}\right) \tag{5}$$

to find c_{ij} and d_{ij}, the dipole-dipole and dipole-quadrupole coefficients for the van der Waals interaction between ions i and j.

TABLE I. Interionic distance and refractive indices at various wavelengths of the alkaline-earth chalcogenides. $C=656.3$ nm, $D=589.3$ nm, $F=486.1$ nm, $Tl=535.1$ nm.

	r_0 (Å)	Refractive indices at indicated wavelengths			n_∞
MgO	2.102	1.7335 *C*	1.7366 *D*	1.7475 *F*	1.7158
CaO	2.406	1.833 *C*	1.837 *D*	1.846 (530 nm)	1.8076
SrO	2.580	1.856 *C*	1.870 *D*	1.880 (535 nm)	1.8094
BaO	2.762	1.958 *C*	1.980 *D*	2.002 (520 nm)	1.8863
MgS	2.595	2.254 *C*	2.271 *D*	2.285 *Tl*	2.1935
CaS	2.84	2.120 *C*	2.137 *D*	2.161 *Tl*	2.0376
SrS	2.935	2.087 *C*	2.107 *D*	2.122 (540 nm)	2.0143
BaS	3.175	2.140 *C*	2.155 *D*	2.183 *Tl*	2.0524
CaSe	2.955	2.245 *C*	2.274 *D*	2.292 (555 nm)	2.1267
SrSe	3.115	2.190 *C*	2.220 *D*	2.252 (540 nm)	2.0597
BaSe	3.31	2.230 (675 nm)	2.268 *D*	2.289 (560 nm)	2.1005
SrTe	3.235	2.367 *C*	2.408 *D*	2.460 *Tl*	2.1814
BaTe	3.493	2.379 *C*	2.440 *D*	2.520 *Tl*	2.0969

2. RESULTS

Thirteen alkaline-earth chalcogenides have been considered, all of which have the NaCl-type crystal structure. Table I lists the experimental values used. All the interionic distance r_0 data are from Wyckoff's[12] compilation and the refractive indices n are from Winchell and Winchell.[13] The values of n_∞ have been found by fitting, by the method of least squares, the data in the three previous columns of the table to the Cauchy relation $n=A+B/\lambda^2$.

Following the TKS approach, the ion polarizabilities were computed by minimizing

$$F_1=\sum_1^N(\alpha_m-\alpha_i-\alpha_j)^2, \tag{6}$$

where $N=13$ is the number of salts considered, using

TABLE II. Computed values of ion polarizabilities (Å^3).

	Mg^{2+} (fixed)	Ca^{2+}	Sr^{2+}	Ba^{2+}	O^{2-}	S^{2-}	Se^{2-}	Te^{2-}
$\alpha(F_1,n_D)$	0.094	1.107	1.746	3.685	1.694	4.746	6.285	8.594
$\alpha(F_1,n_\infty)$	0.094	1.033	1.667	3.277	1.675	4.549	5.796	7.426
$\alpha(F_2,n_D)$	0.094	1.211	1.923	3.514	1.693	4.711	6.186	8.452
$\alpha(F_2,n_\infty)$	0.094	1.157	1.795	3.188	1.657	4.497	5.686	7.375

---

[4] D. W. Lynch, J. Phys. Chem. Solids **28**, 1941 (1967).

[5] H. R. Philipp and H. Ehrenreich, Phys. Rev. **131**, 2016 (1963).

[6] F. Hajj, J. Chem. Phys. **44**, 4618 (1966).

[7] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).

[8] A. F. Ruffa, Phys. Rev. **130**, 1412 (1963).

[9] A. F. Ruffa, Phys. Rev. **133**, A1418 (1964).

[10] L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

[11] J. E. Mayer, J. Chem. Phys. 1, 270 (1933).

[12] R. Wyckoff, *Crystal Structures* (Wiley-Interscience, Inc., New York, 1961), Vol. I.

[13] A. A. Winchell and H. Winchell, *Optical Properties of Artificial Minerals* (Academic Press, Inc. New York, 1964), 3rd ed.

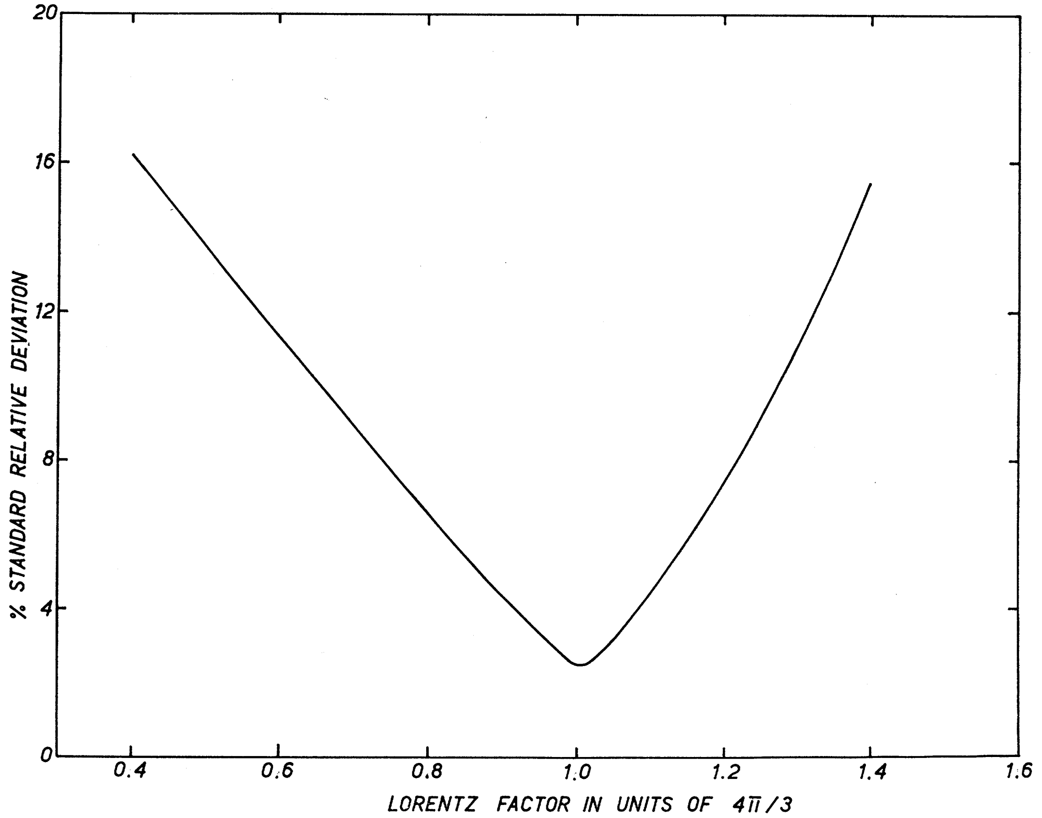

FIG. 1. Graph of standard relative deviation against Lorentz factor for minimization of F_2 and using n_∞ data (i.e., results corresponding to the fourth line of Table II).

both the refractive indices found by extrapolating to zero wavelength and those measured at the wavelength of the sodium D line. The results are presented in the first two lines of Table II. Table III gives the percentage relative deviation of $\alpha_i+\alpha_j$ from α_m for the n_∞ set. The minimum value of F_1 does not completely define the polarizabilities, as if each alkaline-earth ion value is raised by a constant amount while each chalcogenide value is lowered by the same amount the minimum of F_1 is unchanged. Therefore, one polarizability must be fixed by other considerations. In this work, the Mg^{2+} polarizability is taken to be 0.094 Å^3, the value found for the gaseous ion by Pauling.[10] However, this particular ion has a value so much smaller than the other seven ions in the family that even a 100% error in its value would have little effect on the values for the other ions.

The standard relative deviation for the family, given by

$$F_2=\left[\frac{1}{N}\sum_1^N\left(\frac{\alpha_m-\alpha_i-\alpha_j}{\alpha_m}\right)^2\right]^{1/2} \qquad (7)$$

has been calculated and is 3.86% for n_D and 3.12% for n_∞. These are remarkably low values compared with the value of 7.1% given by TKS's polarizabilities for the alkali halides.

Pirenne and Kartheuser suggested that the minimization of the function F_1 gives proportionally too much importance to the fitting of the heavier salts of a family and that the polarizabilities should be found by minimizing the standard relative deviation F_2. This alternative procedure has been carried through to give the results in the third and fourth lines of Table II with the percentage relative deviation of $\alpha_i+\alpha_j$ from

TABLE III. Relative deviation of $\alpha_i+\alpha_j$ from α_m for α_i's evaluated by minimizing F_1 and using n_∞ data.

	O^{2-}	S^{2-}	Se^{2-}	Te^{2-}
Mg^{2+}	−1.5%	+0.55%	···	···
Ca^{2+}	+5.41%	+0.37%	−2.62%	···
Sr^{2+}	+5.48%	−2.01%	+0.44%	−1.15%
Ba^{2+}	−6.95%	+0.96%	+1.53%	+0.96%

TABLE IV. Relative deviation of $\alpha_i+\alpha_j$ from α_m for α_i's evaluated by minimizing F_2 and using n_∞ data.

	O^{2-}	S^{2-}	Se^{2-}	Te^{2-}
Mg^{2+}	−0.45%	+1.67%	···	···
Ca^{2+}	+1.71%	−0.91%	−2.84%	···
Sr^{2+}	+2.37%	−3.26%	+0.20%	−1.93%
Ba^{2+}	−4.64%	+2.74%	+3.69%	−2.33%

TABLE V. Characteristic energies of ions and the van der Waals coefficients between pairs of like ions.

	$\bar{E}$ (eV)	$C_{\pm\pm}$ (eV Å^6)	$d_{\pm\pm}$ (eV Å^8)
Mg^{2+}	83.7	0.555	0.227
Ca^{2+}	23.9	24.0	34.4
Sr^{2+}	19.2	46.3	82.9
Ba^{2+}	14.4	110	261
O^{2-}	19.9	41.0	70.7
S^{2-}	12.1	184	520
Se^{2-}	10.8	261	832
Te^{2-}	9.4	386	1400

TABLE VI. van der Waals coefficients for cation-anion pairs.

	C_{+-} (eV Å^6)	d_{+-} (eV Å^8)		C_{+-} (eV Å^6)	d_{+-} (eV Å^8)
Mg^{2+}-O^{2-}	3.76	4.01			
Ca^{2+}-O^{2-}	31.2	49.3	Ca^{2+}-Se^{2-}	73.2	169
Sr^{2+}-O^{2-}	43.6	76.6	Sr^{2+}-Se^{2-}	106	263
Ba^{2+}-O^{2-}	66.2	136	Ba^{2+}-Se^{2-}	167	466
Mg^{2+}-S^{2-}	6.70	10.9			
Ca^{2+}-S^{2-}	62.7	134			
Sr^{2+}-S^{2-}	89.8	208	Sr^{2+}-Te^{2-}	126	341
Ba^{2+}-S^{2-}	141	369	Ba^{2+}-Te^{2-}	201	605

α_m for the n_∞ set in Table IV. The corresponding standard relative deviations are 3.04 and 2.53%, for the n_D and n_∞ sets, respectively.

The normal Lorentz factor of $L=\frac{4}{3}\pi$ is calculated (e.g., Born and Huang[14]) by considering the ions as independent dipoles. If, on the other hand, the charge clouds of neighboring ions overlapped substantially, a smaller value of L would be appropriate. Figure 1 shows the variation of F_2 for the n_∞ data with a variable Lorentz factor. It clearly indicates that these data are best fitted with the normal value of $\frac{4}{3}\pi$, thus giving further evidence for the appropriateness of the model.

The van der Waals constants were computed by using Eqs. (3)–(5) and are set out in Tables V and VI. Following Lynch[4] and Philipp and Ehrenreich,[5] it is assumed that only the six p electrons of each ion contribute to the refractive index, and so $n=6$ for all ions. The only other published values of van der Waals constants for these materials, which are about a factor of 5 smaller, are those of Huggins and Sakamoto,[15] who used a method of extrapolating from the constants for the isoelectronic ions in the alkali halides.

3. CONCLUSIONS

The Born model of an ionic solid is a good representation of the alkaline-earth chalcogenides to the extent that acceptable ion polarizabilities and van der Waals constants can be calculated for the family of salts. The two criteria of (i) an additivity law for the molar refractions and (ii) a Lorentz internal field factor of $\frac{4}{3}\pi$ are well satisfied. Similarly, it has been found that acceptable ionic radii can be assigned to the individual ions in the alkaline-earth chalcogenides (Boswarva[16]).

The assumption of constancy of one group of ion polarizabilities in different families leads to false conclusions about the polarizability of individual ions within a family. For example, TKS's assumptions (i) halide polarizabilities have the same values in alkali halides and alkaline-earth halides, (ii) the alkaline-earth polarizabilities have the same values in the alkaline-earth halides and the alkaline-earth chalcogenides, gave the O^{2-} polarizability varying between 1.6 and 3.0 Å^3 in the alkaline-earth chalcogenides, contrary to the results of this paper. Conversely, if we make the analogous assumptions from the starting point of the alkaline-earth chalcogenides, namely, (i) the chalgenide polarizabilities have the same values in the alkaline-earth chalcogenides and the alkaline chalcogenides, (ii) the alkali polarizabilities have the same values in the alkali chalcogenides and the alkali halides, we would get the F^- polarizability varying between 0.4 and 0.9 Å^3 in the alkali halides, contrary to TKS's results.

ACKNOWLEDGMENTS

The author wishes to thank all the members of the Physical Properties Section of the Inorganic Materials Division, National Bureau of Standards, Washington, D. C., for their hospitality while this work was carried out. He is also indebted to Dr. H. Bennett, Dr. A. D. Franklin, and Dr. J. B. Wachtman, Jr., of that group for stimulating discussions.

---

[14] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954), p. 101.

[15] M. L. Huggins and Y. Sakamoto, J. Phys. Soc. Japan **12**, 241, (1957).

[16] I. M. Boswarva, J. Phys. C **1**, 582 (1968).