PHYSICAL REVIEW B VOLUME 24, NUMBER 12 15 DECEMBER 1981

Empirical relationship between effective ionic charges and optical dielectric constants in binary and ternary cubic compounds

Kunio Wakamura
Department of Fundamental Natural Science, Okayama College of Science, Ridai-cho, Okayama-city, 700, Japan

Toshihiro Arai
Institute of Applied Physics, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaragi, 305, Japan

(Received 23 January 1981)

The effective ionic charge Z^*e of each ion is determined within a narrow variable range for cubic and near-cubic ternary compounds. The Szigeti effective charge e_s^* [$= 3\sqrt{\epsilon_\infty} Z^* e/(\epsilon_\infty + 2)$] is also evaluated for the anion from the value Z^*e by using the observed optical dielectric constant ϵ_∞. The correlation between e_s^* and the dielectric constant ϵ_∞ is empirically found for many kinds of binary and ternary compounds as $\epsilon_\infty - 1 = 2.0/[(e_s^*/Z_{\rm eff}e) + (e_s^*/Z_{\rm eff}e)^2]$. The value $Z_{\rm eff}$ indicates the effective chemical valency. In the correlation, the relatively large scatter for some compounds is explained by the d- or f-electron effect on the dielectric constant ϵ_∞, and by the screening and the anisotropic effects on the effective charge. From these results, the applicable ranges of the equation used and of the localized effective charge are discussed.

I. INTRODUCTION

The parameters characterizing the dielectric properties have been discussed from the viewpoints of the stability of crystal structure, chemical bonding, elastic properties, etc.[1-7] Effective ionic charge is considered one of them. Besides the effective charges obtained from the calculation of lattice dynamics as fitting parameters, several kinds of effective ionic charges have been discussed by some authors, for instance, Szigeti, Cochran, Kurosawa, etc.[8-10] The relations among the several kinds of effective charges have been proposed.[1,11-14] The transverse effective charge e_T^* is decomposed into the local and the nonlocal parts, e_l^* and e_n^*.[15] The value e_n^* represents the overlapping part in e_T^*, which extends to outside the unit cell and experiences the macroscopic electric field rather than the local effective field.

The effective ionic charge is also divided into the static and dynamic parts.[15,16] The static ionic charge based on the electronegativity is influenced by the symmetry of surrounding atoms. The dynamic ionic charge induced by the lattice vibration depends strongly on the structure of vibrational mode. The Szigeti effective charge e_s^* which is related to e_T^* as $e_s^* = 3e_T^*/(\epsilon_\infty + 2)$ has been discussed from these aspects.[14,16] For binary cubic compounds, it is obtained from the frequencies of transverse ($\omega_{\rm TO}$) and longitudinal ($\omega_{\rm LO}$) modes by the well-known equation[8]

$$(\omega_{\rm LO}^2 - \omega_{\rm TO}^2)^{1/2}[3/(\epsilon_\infty + 2)](\epsilon_\infty \epsilon_v \mu V)^{1/2} = e_s^* , \qquad (1)$$

where μ, V, and ϵ_v and ϵ_∞ stand for the reduced mass, the volume occupied by a chemical formula unit, and the dielectric constant in vacuum and in the high-frequency region, respectively.

The linear relationships have been reported among the effective ionic charges,[15,17] dielectric constant ϵ_∞,[15] Phillips's ionicity scale f_i,[13,15,18] the electronegativity difference per plasma frequency of valence electron $C/\hbar\omega_p$,[11] etc.[1] The validity of these correlations, however, has been limited to only simple binary compounds since the presence of some kinds of cations in a unit cell in other kinds of compounds makes the determination of those values difficult.

In spite of this difficulty, some dielectric parameters were recently determined for ternary compounds. Levine[19] treated the ionicity of each ion in some ternary compounds by introducing the concept of bond polarizability proposed by Phillips and Van Vechten.[20] He obtained the smooth curve of f_i against $b\Delta Z$, where b and ΔZ indicate the prescreening factor of heteropolar part in the averaged energy gap and the difference of the number of valence electrons between the cation and the anion, respectively. Scott determined the effective ionic charge Z^*e of each ion in $\rm AlPO_4$ by extending the equation derived by Cochran[9] and by using the characteristic properties of the compound.[21] The charge Z^*e relates to the Szigeti effective charge e_s^* as $Z^*e = e_s^*(\epsilon_\infty + 2)/3\sqrt{\epsilon_\infty}$. Gervais also determined such charge for some of perovskites and pointed out empirically the linear relation between the charge normalized by the effective chemical valency, $Z^*e/Z_{\rm eff}$, and $\exp(f_i)$ for some binary and ternary compounds.[18] However, the parameters and the correlations mentioned above have been treated for few number of ternary compounds. To investigate the dielectric properties of ternary compounds, the determination of

Z^*e for more compounds and the establishment of a correlation among many dielectric parameters are important.

Our purpose of this paper is to determine Z^*e and to emphasize the correlation between $e_s^*/Z_{\rm eff}e$ and ϵ_∞ for binary and ternary compounds. The Gervais procedure[18] is improved by utilizing the crystal property in this paper. In Sec. II, the effective charges are calculated within a reasonable error for cubic and near-cubic ternary compounds such as spinels, perovskites, and chalcopyrites. In Sec. III, the correlation between the macroscopic dielectric constant ϵ_∞ and the effective charge e_s^* is found empirically for many binary compounds and for the anions of ternary cubic and near-cubic compounds. From the correlation, the applicable range of the equation used above will be discussed. The relatively large scatter in the correlation is discussed from the viewpoints of the screening effect due to valence electrons, of anisotropy in effective field, and of the energy level in electronic orbit.

II. DETERMINATION OF EFFECTIVE CHARGES

The magnitude of the effective charge for a binary compound is determined simply from the equations of motion of ions for longitudinal and transverse directions and the condition of charge neutrality in crystal. For a ternary compound $A_pB_qX_r$, the equation extended by Scott[21] is

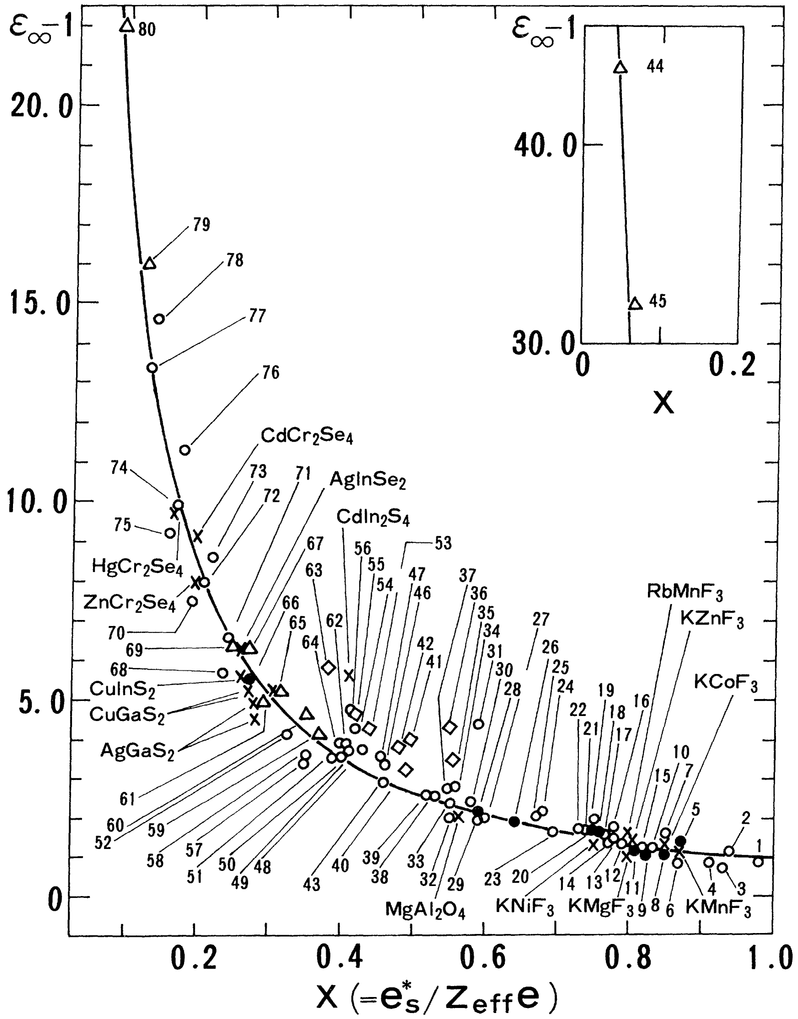

FIG. 1. Relationship between the effective charge normalized by the effective chemical valency, $e_s^*/Z_{\rm eff}\,e$, and $\epsilon_\infty - 1$. □: the $3d$- or $4f$-electron compounds. △: the values calculated from e_T^*. ●: the compounds of types AX_2, and A_2X and ammonium halides. ○: other binary compounds. ×: ternary compounds. The correspondence between the compound and the number is listed on Table III. The solid line shows the relation of $\epsilon_\infty - 1 = 2.0/(x+x^2)$.

$$\sum_j (\omega_{jLO}^2 - \omega_{jTO}^2) = \sum_k \frac{(Z^*e)_k^2/m_k}{\epsilon_v V}, \qquad (2)$$

where j is taken over all infrared-active optical modes and k over atoms in the unit cell. The frequencies of jth longitudinal and transverse modes, volume, atomic mass, and the dielectric constant in vacuum are indicated by ω_{jLO}, ω_{jTO}, V, m, and ϵ_v, respectively. The effective charge of ion A is denoted by Z_A^*e.

In the derivation of this equation, Cochran's equation,[9] which is derived under the condition of isotropic effective field, is used. Strictly speaking, this condition should be satisfied whenever Eq. (2) is applied. In cubic binary compounds, each ion is surrounded by the isotropic effective field. However, each ion in cubic ternary compounds is not necessarily surrounded by the isotropic field. For instance, each anion in a spinel AB_2X_4 is surrounded by three octahedrally coordinated cations B and one tetrahedrally coordinated cation A. Furthermore, each anion in a perovskite fluorite ABF_3 is surrounded by four cations A in the plane perpendicular to the B-F axis and two cations B in the direction parallel to the axis. Although the straightforward application of Eq. (2) to these compounds is questionable by the reason of this anisotropic field, we make it possible by assuming tentatively that the effective field around the anion is isotropic as the result averaged over all surrounded cations. By this assumption, the same kinds of atoms in a unit cell have a same value of charge Z^*e, and the condition of charge neutrality in a unit cell is written as

$$pZ_A^* + qZ_B^* - rZ_X^* = 0. \qquad (3)$$

The validity of the assumption is suggested from the fact that the calculated values make one smooth curve as shown in Fig. 1. As three kinds of positive unknown values Z^* are included in Eqs. (2) and (3), we cannot determine each value of Z^* from both equations. However, if we substitute an assumed value Z_A^* into both equations, charges Z_B^*e and Z_X^*e are determined from these equations. In order to determine the values Z_B^*e and Z_X^*e within a narrow variable range, the restriction on the variable range of Z_A^* is introduced.

Gervais restricted the magnitude of Z_A^* by the condition that the value in the square root which is included into the equation obtained by combining Eqs. (2) and (3) must be positive.[18] The charges Z_B^*e and Z_X^*e in the ternary compounds including the alkali or alkali earth element were determined by this condition within a narrow variable range in spite of the wide variation of Z_A^*e. However, the values for other kinds of compounds are not determined within a narrow variable range from this condition. Therefore we note here the result that, of the two kinds of cations in a ternary compound, one cation has a normalized effective charge that is larger than another cation. When this inequality between Z_A^*e/Z_{eff}^A and Z_B^*e/Z_{eff}^B is introduced, the variable range of the magnitude of charge Z_A^*e can be decreased about one-half of that limited by the condition used by Gervais, where the effective chemical valency of ion A is indicated by Z_{eff}^A. The upper or lower limits of charges Z_A^*e for spinels or other ternary compounds are determined from this consideration. The inequality for each compound is determined as follows.

In spinels $A^{+2}B_2^{+3}X_4^{-2}$, the normalized effective charge of cation B is considered to be larger than that of cation A for two reasons. One reason is that the zinc-blende interionic bond in a spinel is predominantly covalent when the size of cation A is larger, and the pure ionic force places a cation B in the interstices of the largest anion coordination, viz., the octahedral positions.[22] Another reason is that the splitting of LO and TO mode frequencies for the two infrared-active modes in lower energy is smaller than that for the two modes in higher energy, and each of the two modes relates strongly to the cations A and B, respectively.[23] According to the correspondence between the splitting and the effective charge, the inequality is concluded. The same inequality was also suggested by Lauwars *et al.*[24] and Brüesch *et al.*[25] Brüesch's model includes only short-range forces. The magnitudes of the force constants between A and X ions are about twice of those between B and X ions in selenide spinels. When the proportional relation of the force constant with the covalency is considered,[3,5] this difference in the magnitudes of force constants is due to the fact that the ionicity of cation B is larger than that of cation A.

In perovskite fluorites $A^{+1}B^{+2}F_3^{-1}$, the normalized effective charge Z_A^*e/Z_{eff}^A is considered to be larger than that of Z_B^*e/Z_{eff}^B from the following consideration. Perry and Young[26] assigned the highest, the middle, and the lowest frequency modes to F_2-B-F_2 stretching, F_1-B-F_1 bending, and BF_3-A ion modes, respectively. Furthermore, they have concluded that the effective charges for the two modes in high-frequency side are smaller than that of the lowest mode under the assumption of independence of each vibration in the three infrared-active modes. As each normal mode includes only one kind of cation, the conclusion mentioned above is derived from these results.

In chalcopyrite-type compounds $A^{+1}B^{+3}X_2^{-2}$, we can conclude that the normalized effective charge of cation A is larger than that of cation B, because the behaviors of B_2 and E_u vibrational modes each having highest frequency can be explained by assuming that the covalency of the B-X bond is larger than that of the A-X bond.[27] This assumption is derived from the magnitudes of bond dielectric constants for A-X and B-X bonds, which were defined by Levine.[19] That is, the bond dielectric constant for the B-X bond is larger than that for the A-X bond.

Although the chalcopyrite structure is not cubic, it possesses approximately a zinc-blende structure as the fundamental unit. Furthermore, the dielectric constant ϵ_∞ for the parallel and perpendicular directions to C axis are almost of the same magnitude in spite of the large difference of the lattice constants between both directions. So we consider them as nearly cubic in the dielectric properties.

Values of opposite ends, that is, the lower or upper limits of the values Z_A^*e/Z_{eff}^A for the spinels or other compounds, are assumed not to exceed the lowest or highest magnitude in the normalized effective charges of usual binary compounds. The assumption is made because the cation charges in the ternary compounds showed a feature similar

TABLE I. The effective charge Z^*e of each ion and Szigeti effective charges for anions in spinels and perovskites. The values of Z_{eff} are 2.0, 3.0, and 2.0 for the elements A, B, X in spinels, respectively, and those of perovskites are 1.0, 2.0, and 1.0, respectively. The data for the perovskites and the lattice constants of spinels are taken from Refs. 26, a, and b.

Compound	Element	Z^*/Z_{eff}	$e_s^*/Z_{\text{eff}}e$	ϵ_∞
		Spinel structure		
$ZnCr_2Se_4$[c]	Zn	0.08–0.25		9.0
	Cr	0.26 ± 0.02		
	Se	0.24 ± 0.01	0.20 ± 0.01	
$CdCr_2Se_4$[c]	Cd	0.08–0.27		10.2
	Cr	0.28 ± 0.01		
	Se	0.25 ± 0.01	0.20 ± 0.01	
$HgCr_2Se_4$[c]	Hg	0.08–0.23		10.8
	Cr	0.24 ± 0.01		
	Se	0.22 ± 0.01	0.17 ± 0.01	
$CdIn_2S_4$[d]	Cd	0.10–0.45		6.6
	In	0.52 ± 0.05		
	S	0.46 ± 0.02	0.41 ± 0.02	
$MgAl_2O_4$[e]	Mg	0.10–0.55		3.0
	Al	0.61 ± 0.05		
	O	0.54 ± 0.02	0.56 ± 0.02	
		Perovskite structure		
$KNiF_3$	K	0.70–0.97		2.30
	Ni	0.65 ± 0.06		
	F	0.71 ± 0.005	0.75 ± 0.005	
$KMnF_3$	K	0.82–0.96		2.10
	Mn	0.79 ± 0.03		
	F	0.83 ± 0.01	0.88 ± 0.001	
$KCoF_3$	K	0.80–0.95		2.25
	Co	0.76 ± 0.04		
	F	0.80 ± 0.001	0.85 ± 0.001	
$KZnF_3$	K	0.76–0.95		2.34
	Zn	0.71 ± 0.05		
	F	0.76 ± 0.001	0.80 ± 0.001	
$KMgF_3$	K	0.74–0.96		2.04
	Mg	0.70 ± 0.04		
	F	0.75 ± 0.01	0.80 ± 0.01	
$RbMnF_3$	Rb	0.75–0.98		2.53
	Mn	0.71 ± 0.04		
	F	0.76 ± 0.01	0.80 ± 0.01	

[a] P. K. Baltzer, H. W. Lehmann, and M. Robbins, Phys. Rev. Lett. 13, 493 (1965).

[b] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1963).

[c] K. Wakamura, T. Arai, and K. Kudo, J. Phys. Soc. Jpn. 40, 1118 (1976).

[d] K. Yamamoto, T. Murakawa, Y. Ohbayashi, H. Shimizu, and K. Abe, J. Phys. Soc. Jpn. 35, 1258 (1973).

[e] M. E. Striefler and S. L. Boldish, J. Phys. C 11, L237 (1978).

TABLE II. The effective charge Z^*e of each ion and Szigeti effective charges for anions in chalcopyrite-type compounds. The magnitudes of lattice constants are taken from Wyckoff.[a] The values of $Z_{\rm eff}$ are 1.0, 3.0, and 2.0 for the elements A, B, and X, respectively.

Compound	Element	$Z^*/Z_{\rm eff}$	$e_s^*/Z_{\rm eff}e$	ϵ_∞
$CuGaS_2$[b,c]	Cu	0.34–0.90		6.2
$(\vec{E}\parallel c)$	Ga	0.25 ± 0.10		
	S	0.34 ± 0.01	0.31 ± 0.01	
	Cu	0.29–0.86		6.2
$(\vec{E}\perp c)$	Ga	0.20 ± 0.09		
	S	0.30 ± 0.01	0.27 ± 0.01	
$CuInS_2$[d]	Cu	0.30–0.84		6.6
$(\vec{E}\parallel c)$	In	0.20 ± 0.10		
	S	0.29 ± 0.01	0.26 ± 0.01	
$AgGaS_2$[b]	Ag	0.29–0.90		5.5
$(\vec{E}\parallel c)$	Ga	0.20 ± 0.09		5.9
$(\vec{E}\perp c)$	S	0.30 ± 0.01	0.28 ± 0.01	
$AgInSe_2$[e]	Ag	0.30–0.90		7.16
$(\vec{E}\parallel c)$	In	0.20 ± 0.10		
	Se	0.30 ± 0.01	0.26 ± 0.01	

[a] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1963).

[b] J. P. van der Ziel, A. E. Meixner, H. M. Kasper, and J. A. Ditzenberger, Phys. Rev. 139, 4286 (1974).

[c] J. Baars and W. H. Koschel, Solid State Commun. 11, 1513 (1972).

[d] W. H. Koschel, F. Sorger, and J. Baars, J. Phys. C 3, 177 (1975).

[e] G. Kanellis and K. Kampas, Mater. Res. Bull. 13, 9 (1978).

to the correlations established in the binary compounds, though they have been reported only for a few ternary compounds.[18,28]

The charges calculated with the consideration mentioned above are listed for the cubic- and chalcopyrite-type compounds in Tables I and II, respectively. Only compounds where the observed number of vibrational modes agrees with the number expected from the crystal symmetry are used. In the chalcopyrites, such agreement has been reported for only a few compounds.

Szigeti effective charges e_s^* calculated by using the observed value ϵ_∞ are listed in Tables I and II. In the tables, the magnitudes of effective charges for the cation B in spinels and for the anion X in the all compounds are determined within a very narrow variable range. However, the values of cation B in the perovskites and chalcopyrites are determined within a wide variable range. The decrement of the variable range of Z_A^* decreases the variable ranges of Z_B^* and Z_X^*. In spinels, the procedure of further decreasing the variable range of Z_A^* is reported elsewhere.[28]

III. DISCUSSION

A. Effective charges in binary compounds

1. Correlation with the dielectric constants

To find the correlation between the effective charge and the dielectric constant ϵ_∞, the binary compounds are considered first. Although the linear relations of effective charges e_T^*, e_s^*, and e_l^* to dielectric parameters have been reported for some binary compounds, the deviation from linearity and the spread of scatter of each calculated point are not so small in some cases.[11,15,18] In order to explain the cause of this and to investigate the dielectric properties systematically from the point of view of effective charge or ionicity, we consider the connection between the susceptibility χ and the effective charge e_s^*. Figure 1 shows the relationship between $e_s^*/Z_{\rm eff}e$ and $\epsilon_\infty - 1$ for the cubic and nearly cubic binary compounds. For the compounds having the small magnitudes of $e_s^*/Z_{\rm eff}e$ and a part of wurtzite- and zinc-blende-type II-VI compounds, the values e_s^* are calculated from e_l^* and plotted with the triangles. The reason that e_l^* is employed will be explained in Sec. III A 3.

Most points in Fig. 1 are plotted on one smooth curve. The curve is expressed as

$$\epsilon_\infty - 1 = 2.0/(x + x^2)\,, \tag{4}$$

where x indicates the normalized Szigeti effective charge, $e_s^*/Z_{\rm eff}e$. Good agreements are seen for the compounds which contain elements of the first row in the Periodic Table, such as SiC, BN, and AlN. These compounds, however, show a large deviation in the relations of $e_s^*/Z_{\rm eff}e$ versus $C/\hbar\omega_p$, $\exp(f_i)$ versus $(Z^*/Z_{\rm eff})$, etc.[1,11,18]

As most points show a small scatter from the curve, the applicability of Eq. (4) to a greater number of compounds may be supported intensely. The reason for this good agreement may be due to the cancellation of some terms included in $(\epsilon_\infty - 1)$ and e_s^*, though the effective charge e_s^* $[= 3e_T^*/(\epsilon_\infty + 2)]$ includes ϵ_∞ as the shielding effect due to the valence electrons. The relatively large scatter, however, is found in Fig. 1 for the compounds of three groups. The reasons for scatter will be described in Secs. III A 2, A 3, and A 4.

2. Influence of 3d and 4f electrons

One group with $3d$ or $4f$ electrons, such as MnO, NiO, EuO, EuSe, etc., is plotted as squares in Fig. 1. The large scatter for the compounds with $3d$ electrons has also been found in the relations $\exp(f_i)$ versus $Z^*/Z_{\rm eff}$, $e_s^*/Z_{\rm eff}e$ versus $C/\hbar\omega_p$, etc., and has been considered to be due to the presence of the d-electron band near or at the top of the valence band.[11,18,44] Levine discussed the susceptibility χ of the transition-metal compounds possessing unfilled d shells by introducing the parameter Γ, which was defined for a compound as the number of d holes in a compound divided by the number of valence electrons in a compound.[44]

The value Γ describes the fractional increase of χ; that is, the dielectric constant ϵ_∞ for the compound having a large Γ includes a large contribution from the $3d$ electron. In Fig. 1, the relation between Γ and the deviation from the solid line is found, that is, the large deviation is seen for compounds having large Γ such as MnS ($\Gamma = 0.38$) and MnO ($\Gamma = 0.38$) and the small deviation for such compounds having the small Γ such as NiO ($\Gamma = 0.12$) and CoO ($\Gamma = 0.20$). Furthermore, the shift of the value $Z_{\rm eff}$ from a formal chemical valency to a larger value has been considered as originating from the d electron. Lawaetz[11] obtained good regularity in the relation between $e_s^*/Z_{\rm eff}e$ and $C/\hbar\omega_p$ by postulating the shifted value $Z_{\rm eff} = 1.5$ instead of $Z_{\rm eff} = 1.0$ for Cu and Ag halides. Similar effective valency for these halides and the alkaline-earth sulfides MS (M = Ca, Ba, Sr), $Z_{\rm eff} = 1.5$, has also been employed in such correlations as c/a versus $(Z_{\rm eff}C/\hbar\omega_p)^2$ and c/a versus $Z_{\rm eff}^2 f_i/\epsilon_\infty$,[4,13] where a and c describe the lattice constants of wurtzite-type compounds for the A_u and E_u directions. These effective valencies are also employed in Fig. 1; they decrease the deviation from the solid line for these halides.

In the transition-metal and rare-earth compounds, similar procedures will make the deviation decrease since the energy levels of $3d$ and $4f$ electronic orbits are similar to the case of Cu and Ag halides. As a matter of fact, the decrement of deviation is obvious by considering that the points deviating upward from the solid line will be shifted to the lower value of $(e_s^*/Z_{\rm eff}e)$ by increasing the magnitude of $Z_{\rm eff}$. The values of $Z_{\rm eff}$ expected to lie on the solid line are shown in parentheses in Table III. From these values, the effective chemical valencies of those $3d$ and $4f$ electron compounds, whose formal chemical valencies are 2.0, are expected to be between 2.5 and 3.0.

3. *Influence of screening effects*

In compounds having large values of ϵ_∞ and some wurtzite- and zinc-blende-type II-VI compounds such as CdSe, GaN, and ZnTe, the scatter of effective charges is also large, as shown in parentheses in Table III. The large scatter of these compounds is also found in the relationships $e_s^*/Z_{\rm eff}e$ versus $C/\hbar\omega_p$ and $\exp(f_i)$ versus $Z^*/Z_{\rm eff}$.[11,18] The increase of the nonlocal part of the effective charge is expected for compounds having a large

TABLE III. Correspondence between the numbers and the compounds.

Compound	No.	Ref.	Compound	No.	Ref.
		Crystals with the NaCl arrangement			
		Alkali halides			
LiF	6	11,15	KCl	15	15
LiCl	22	11,15	KBr	14	15
LiBr	24	11,15	KI	21	15
LiI	34	31	RbF	1	15
NaF	3	11,15	RbCl	10	15
NaCl	13	15	RbBr	12	15
NaBr	23	11,15	RbI	17	15
NaI	19	11,15	CsF	2	29
RF	4	11,15			
		Alkaline oxides, sulfides			
MgO	27	11,15	CaS	58	35
CaO	33	15	SrS	57	35
SrO	30	15	BaS	50	35
		Eight-electron, non-rare-gas configuration			
AgF	29	30	AgBr	47	15
AgCl	43	15	CdO	31	15
		Ten-electron, non-rare-gas configuration			
PbS (0.38)	79	15	PbTe (0.28	45	15
PbSe (0.35)	80	15	SnSe (0.26)	44	15
		3d electron compounds			
CoO (2.6)	53	38	MnO (2.8)	35	37
NiO (2.6)	55	38	MnS (2.8)	63	36
		4f electron compounds			
EuO (3.3)	36	39	EuSe (2.4)	42	39
EuS (2.7)	41	39	EuTe (2.3)	40	39,40
		Others			
LiH	39	32	LiD	38	31,32
		Crystals with the CsCl arrangement			
CsCl	7	11,15	TlBr	54	15
CsBr	16	11,15	NH_4Cl	20	43
CsI	25	11,15	NH_4Br	26	43
TlCl	48	15			
		Crystals with the ZnS arrangement			
AgI	62	15	AlP	71	15
CuCl	64	15	AlAs	72	15
CuBr	46	11,15	AlSb	75	15
CuI	52	33,15	GaP	70	15
ZnS (0.45)	59	15	GaAs	74	15
ZnSe (0.38)	61	15	GaSb	77	15
ZnTe (0.32)	67	15	InP	73	15
CdTe (0.38)	69	15	InAs	76	15
BN	51	15	InSb	78	15
SiC	68	11,15			
		Crystals with the ZnO arrangement			
AlN	49	11,15	CdSe (0.41)	65	15
GaN	56	15	ZnO	37	11,15
CdS (0.45)	60	15	BeO	32	11,15
		Cubic fluorite structure			
CaF_2	9	34	CdF_2	5	34
SrF_2	8	34	$SrCl_2$	18	41
BaF_2	11	34			
		Others			
Cu_2O	66	42	Al_2O_3	28	18

value of ϵ_∞ because the weak bounded electrons contributing to the nonlocal part may be polarized easily by the applied electric field and hence may induce a large magnitude of ϵ_∞. Therefore we calculate e_s^* by using e_l^* instead of e_T^*.[15] The calculated values from this process are shown by triangles in Fig. 1. The magnitudes calculated from e_T^* are also indicated in parentheses in Table III. The deviation from the solid line is improved greatly for compounds having ϵ_∞ larger than about 15.

For wurtzite-type compounds, two reasons for the large deviations are considered. One is the crystal anisotropy. However, it will not give at large an influence to the deviations because these compounds have nearly equal magnitudes of ϵ_∞ for A_u and E_u directions.[45] Furthermore, it is also suggested that some of these compounds such as BeO, ZnS, and AlN show the small deviation in Fig. 1.

Another reason is the influence of screening. For wurtzite-type compounds, Brodsky and Burstein have argued that the local part of the susceptibility χ is very small in comparison with the nonlocal part of χ.[46] Furthermore, only wurtzite-type compounds having relatively larger values of ϵ_∞ show the larger deviation. These results suggest also the importance of the nonlocal part in the effective charge. For this reason, the charges e_s^* are also calculated from e_l^*, and the deviation greatly decreases. For the reasons mentioned above, the screening effect due to the interband electronic transitions is considered to be important for compounds having ϵ_∞ larger than about 15 and for some wurtzite- and zinc-blende-type II-VI compounds.

4. *Influence of crystal anisotropy*

Large scatter is also seen for the anisotropic compounds which do not include the elements mentioned in Secs. III A 2 and A 3. To see the trend of the scatter, the effective charges of those compounds are shown in Fig. 2. The scatter is larger in comparison with that of cubic compounds shown in Fig. 1. Since those compounds do not include the kinds of atoms mentioned in Secs. III A 2 and A 3, this large scatter may have originated from crystal anisotropy. As a matter of fact, the Lorentz field calculated from the summation of atomic dipole moments gives different forms for the isotropic and anisotropic crystals.[53] The effective charge calculated by introducing the effective field due to the anisotropic arrangement of ions will indicate a magnitude different from that in Fig. 2. For these reasons, the inadequacy of application of Eq. (2) to the anisotropic crystals is expected.

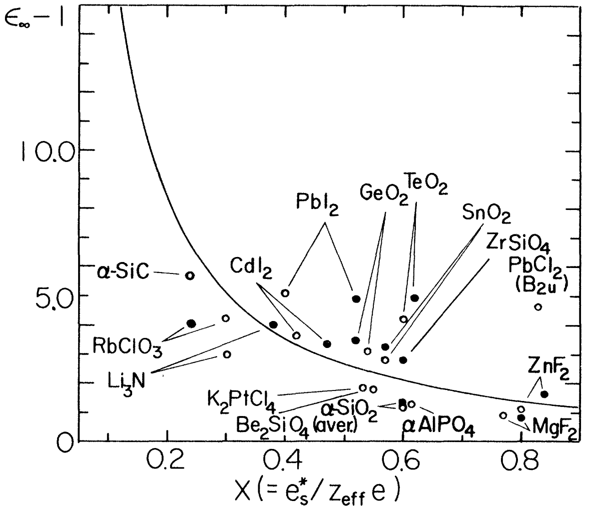

FIG. 2. Relationship between $e_s^*/Z_{\text{eff}}\, e$ and $\epsilon_\infty - 1$ for anisotropic compounds. ● and ○ show the values for the directions parallel and perpendicular to c axis in uniaxial crystals, repsectively. Only $PbCl_2$ is a biaxial crystal. Solid line shows the relation of $\epsilon_\infty - 1 = 2.0/(x + x^2)$. The references of data used for the calculation: SiC (Ref. 15), PbI_2 and CdI_2 (Ref. 47), Li_3N (Ref. 48), $PbCl_2$ (Ref. 49), MgF_2 and ZnF_2 (Ref. 50), K_2PtCl_4 (Ref. 51), α-$AlPO_4$ (Refs. 21 and 52), and others (Ref. 18).

B. Effective charges in ternary compounds

1. *Correlation between effective charge and dielectric constant*

Selenide spinels show nearly equal magnitudes of normalized effective charge $e_s^*/Z_{\text{eff}}e$ ($\simeq 0.2$) for anions and cations. This small value is supported by the model proposed by Brüesch *et al.*, because the model only includes short-range valence forces.[25] In $CdIn_2S_4$, the normalized effective charge is about 0.6 and not so small. Hence the force constants in $CdIn_2S_4$, which are calculated with the Brüesch model, will not give good results. The result reported by Shimizu *et al.*,[54] verifies this.

The dielectric constant ϵ_∞ is an averaged macroscopic value. On the other hand, the effective charge is the value belonging to each ion in a crystal. In a binary cubic compound, the effective charges of the anion and cation have the same absolute value. The dielectric constant also has one value for a binary cubic compound and corresponds to the effective charge as shown in Fig. 1. In a ternary cubic compound, there are three kinds of effective charges belonging to each ion. Which effective charge characterizes the dielectric constant of ternary compound? For this problem, Eq. (4) obtained for binary compounds is not applied directly to the ternary compounds.

Now we plot tentatively the normalized effective charges of anions in ternary compounds as ×'s in Fig. 1. The points fall on the solid line. The effective charges of cations, e_s^*, obtained by using ϵ_∞, however, do not fall on the solid line. Therefore the anion charge in the ternary compound composed of two kinds of cations is considered to relate directly to the macroscopic value of ϵ_∞. For the compounds composed of two kinds of anions, the charge of the cation will be related directly to ϵ_∞. These results are also inferred from considering the two kinds of bonds in the unit cell. The establishment of a chemical bond between two atoms having different electronegativities makes a transfer of electrons between them, namely, the appearance of an effective charge. Each effective charge is characterized with each corresponding bond. In compounds composed of two kinds of cations, the effective charge of the anion is characterized by the bond belonging to each cation. According to Levine's treatment,[19,44] the macroscopic dielectric constant ϵ_∞ is obtained from averaging each bond dielectric constant with the number of nearest-neighbor bonds of the anion. This averaging is similar to the relation between the effective charge of the anion and the bonds mentioned above. Therefore, the effective charge of each cation may correlate to the bond dielectric constant characterized by each cation.

2. *Influence of crystal anisotropy in ternary compounds*

The values $e_s^*/Z_{\rm eff}e$ calculated for anisotropic ternary compounds by the same procedure with the case of the cubic ternary compounds are shown in Fig. 2. Large scatter from the solid line is found for these compounds. The cause of deviation is considered to be similar to the case of binary anisotropic compounds, and the good agreements for isotropic compounds in Fig. 1 suggest the suitability of the idea of the averaging field described in Sec. II. It is also inferred by the following consideration. In cubic ternary compounds, the arrangement of each atom shows cubic symmetry over a unit cell. When we consider nearest-neighbor atoms, the environment of the anion, however, does not necessarily possess cubic symmetry as previously mentioned. As the local electric field at an anion is induced from the dipole moments in the Lorentz spherical cavity composed of a number of unit cells, the averaging of this sphere is related strongly to the symmetry of the atomic arrangement in the crystal and is not related strongly to the symmetry of the nearest neighbor of the anion. This fact induces the large difference between the effective charge of cubic compound having the nonisotropic symmetry around the anion and the effective charge of noncubic compound which has the noncubic symmetry in the atomic arrangement in the unit cell. The large scatter for $CdIn_2S_4$ in Fig. 1 is considered to be related to this symmetry of atomic arrangement, that is, the partial inverse spinel structure.

IV. SUMMARY

This paper has shown a method of calculation for an effective charge within a narrow variable range for the ternary cubic and nearly cubic compounds. An improvement is the application of the result that the magnitude of normalized effective charge of one cation is larger than that of another in two kinds of cations, which is determined from the crystal properties qualitatively investigated. The correlation between the Szigeti effective charge of an anion calculated by this procedure and the dielectric constant ϵ_∞ was empirically determined for spinel, perovskite, and chalcopyrite-type compounds. The correlation was written as $\epsilon_\infty - 1 = 2.0/[(e_s^*/Z_{\rm eff}e) + (e_s^*/Z_{\rm eff}e)^2]$. Using this relation, the following results were obtained. (1) In ternary compounds having one anion, the normalized Szigeti effective charge of the anion corresponds directly to ϵ_∞. (2) The values ϵ_∞ and $Z_{\rm eff}$ (2.5–3.0) increase largely due to the contribution of $3d$ or $4f$ electrons. (3) In compounds having ϵ_∞ values larger than about 15 and in some of wurtzite- and zinc-blende-type II-VI compounds, the nonlocal part of effective charge is important. (4) The magnitudes of Szigeti and Cochran effective charges are influenced strongly by the crystal anisotropy.

---

[1] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).

[2] J. A. Van Vechten, Phys. Rev. 182, 891 (1969).

[3] E. Loh, Phys. Rev. 169, 750 (1968).

[4] P. Lawaetz, Phys. Rev. 35, 4039 (1972).

[5] R. M. Martin, Phys. Rev. B 1, 4005 (1970).

[6] S. S. Mitra and R. Marshall, J. Chem. Phys. 41, 3158 (1964).

[7] A. Navrostsky and J. C. Phillips, Phys. Rev. B 11, 1583 (1975).

[8] B. Szigeti, Trans. Faraday Soc. 45, 155 (1949).

[9] W. Cochran, Adv. Phys. 9, 387 (1960).

[10] T. Kurosawa, J. Phys. Soc. Jpn. 16, 1298 (1961).

[11] P. Lawaetz, Phys. Rev. Lett. 26, 697 (1971).

[12] J. Tateno, J. Phys. Chem. Solids 31, 1641 (1970).

[13] S. A. Wemple, Phys. Rev. B 7, 4006 (1973).

[14] J. P. Suchet, J. Electrochem. Soc. 124, 30C (1977).

[15] G. Lucovsky, R. M. Martin, and E. Burstein, Phys. Rev. B 4, 1367 (1971).

[16] E. Burstein and M. H. Brodsky, Int. J. Quantum Chem. IS, 759 (1967).

[17] G. Lucovsky, R. M. White, W. Y. Liang, R. Zallen, and Ph. Schmid, Solid State Commun. 18, 811 (1976).

[18] F. Gervais, Solid State Commun. 18, 191 (1976).

[19] B. F. Levine, J. Chem. Phys. 59, 1463 (1973).

[20] J. C. Phillips and J. A. Van Vechten, Phys. Rev. 183, 709 (1969).

[21] J. F. Scott, Phys. Rev. 34, 1360 (1971).

[22] J. B. Goodenough and A. L. Loeb, Phys. Rev. 98, 391 (1955).

[23] K. Wakamura, T. Arai, S. Onari, K. Kudo, and T. Takahashi, J. Phys. Soc. Jpn. 35, 1430 (1973).

[24] H. A. Lauwars and M. A. Herman, J. Chem. Phys. Solids 41, 223 (1980).

[25] P. Brüesch and F. D'Ambrogio, Phys. Status Solidi B 50, 513 (1972).

[26] C. H. Perry and E. F. Young, J. Appl. Phys. 38, 4616 (1967).

[27] A. Miller, G. D. Holah, W. D. Dunnett, and G. W. Iseler, Phys. Status Solidi B 78, 569 (1976).

[28] K. Wakamura, T. Ogawa, and T. Arai, Jpn. J. Appl. Phys. 19 Suppl. 19-3, 249 (1980).

[29] J. R. Hardy and A. M. Karo, Phys. Rev. 168, 1054 (1968).

[30] G. L. Bottger and A. L. Geddes, J. Chem. Phys. 56, 3735 (1972).

[31] R. K. Singh, J. Phys. C 7, 3473 (1974).

[32] M. H. Brodsky and E. Burstein, J. Phys. Chem. Solids 28, 1655 (1967).

[33] T. Murahashi and T. Koda, J. Phys. Soc. Jpn. 40, 747 (1976).

[34] D. R. Bosomworth, Phys. Rev. 157, 709 (1967).

[35] M. Droefenik and A. Azman, J. Phys. Chem. Solids 33, 761 (1971).

[36] D. R. Huffman and R. L. Will, Phys. Rev. 156, 989 (1967).

[37] T. B. Kinney and M. O'Keeffe, Solid State Commun. 7, 977 (1969).

[38] P. J. Gielisse, J. N. Plendl, L. C. Mansur, R. Marshall, S. S. Mitra, R. Mykolajewycz, and A. Smakura, J. Appl. Phys. 36, 2446 (1965).

[39] J. D. Axe, J. Phys. Chem. Solids. 30, 1403 (1969).

[40] G. D. Holah, J. S. Webb, R. B. Dennis, and C. R. Pidgeon, Solid State Commun. 13, 209 (1973).

[41] R. Droste and R. Geick, Phys. Status Solidi B 62, 511 (1974).

[42] E. C. Heltemes, Phys. Rev. 141, 803 (1966).

[43] C. H. Perry and R. P. Lowndes, J. Chem. Phys. 51, 3648 (1969).

[44] B. F. Levine, Phys. Rev. B 7, 2591 (1973).

[45] A. Manabe, A. Mitsuishi, and H. Yoshinaga, Jpn. J. Appl. Phys. 6, 593 (1967).

[46] M. H. Brodsky and E. Burstein, Bull. Am. Phys. Soc. 7, 214 (1962).

[47] G. Lucovsky and R. M. White, Nuovo Cimento 38B, 290 (1977).

[48] H. R. Chandrasekhar, G. Bhattacharya, R. Migoni, and H. Bilz, Solid State Commun. 22, 681 (1977).

[49] J. Hiraishi, K. Tani, and T. Tamura, J. Chem. Phys. 71, 554 (1979).

[50] A. S. Barker, Jr., Phys. Rev. 136, A1290 (1964).

[51] J. Hiraishi and T. Tamura, J. Chem. Phys. 66, 3899 (1977).

[52] A. N. Lazarev, N. A. Mazhenov, and A. P. Mirgorodskii, Opt. Spectrosc. 46, 348 (1979).

[53] C. Kittel, *Introduction to Solid State Physics,* 4th ed. (Wiley, New York, 1971), Chap. 13.

[54] H. Shimizu, Y. Ohbayashi, K. Yamamoto, and K. Abe, J. Phys. Soc. Jpn. 38, 750 (1975).