A Pseudopotential Study on Dielectric Theory of Electronegativity and Transverse Effective Charges in Zinc-Blende Structure Binary Compounds

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The parameters of the dielectric theory of electronegativity such as heteropolar gap and ionicity, have been calculated by using pseudopotentials. By analyzing the results obtained, the confidences of the pseudopotentials used are checked. The transverse effective charges have been also calculated. The result suggests the importance of effective valence and effective number of valence electrons in the evaluation of this quantity. Among the binary compounds considered, special emphases have been given to superionic materials. Discussions on how the considered physical quantities are related with the properties of these materials are given.

§1. Introduction

The pseudopotential method has been used quite commonly in the calculation of condensed matter properties. It has been used to study diverse properties in metals, semiconductors and insulators such as structural energies, electronic density of states, phonon spectra, etc.[1] By using the pseudopotential method, the present author performed a comparative study of the bonding nature in binary compounds with the zinc-blende structure.[2,3] There, it has been shown that the real space pseudopotential that reflects the valence electron distribution provides useful information to understand the superionic conducting materials. For instance, it has been shown that the bonding in Cu and Ag halides is determined mainly by anions.[2,3] Such finding provides a microscopic basis to the traditionally adopted picture of superionic conductors, that is, mobile ions in cage formed by immobile ions.[4,5] Recently, a detailed study of the bonding in molten CuI by using *ab initio* methods has been reported.[6] It will be interesting to perform systematic studies of this kind and compare with the finding of pseudopotential studies.

The dielectric theory of electronegativity introduced by Phillips and Van Vechten provides an approach to characterize the bonding nature of solids.[7,8] It has been used widely to study the chemical trends of materials properties.[7-10] Focusing on superionic materials, an analysis of the theory has been performed previously.[11]

Another quantity of fundamental importance in the lattice dynamical, optical and dielectric properties of solids is the transverse effective charge. Since it is a quantity intimately related with the bonding nature of the materials and is measurable experimentally, its study is indispensable for deep understanding of materials properties. Concerning effective charges in superionic materials, some studies have been performed.[12-17]

In the present report, the materials parameters that appear in the dielectric

theory of electronegativity and the transverse effective charges are calculated by applying the relationships obtained from an analysis of the pseudopotentials.[3] From the result of the calculation, the confidence of the pseudopotentials[2],[3],[18] and the method[2],[3],[19] used previously are checked.

§2. Real space pseudopotential

The real space pseudopotential $V_{\mathrm{p}}(r)$ is given by[2],[3],[19]

$$V_{\mathrm{p}}(r) = \left(\frac{1}{N_\alpha}\right) \sum_\alpha \sum_G S_\alpha(G) V_\alpha(G) \exp(iG \cdot r) \ , \tag{2.1}$$

where

$$S_\alpha(G) = \exp(-iG \cdot \tau_\alpha) \tag{2.2}$$

is the structure factor and

$$V_\alpha(G) = \left(\frac{N_\alpha}{\Omega}\right) \int dr' v_\alpha(r') \exp(-iG \cdot r') \tag{2.3}$$

is the pseudopotential form factor associated with the α-atom. N_α is the number of basis atoms, Ω is the primitive unit cell volume and τ_α is the basis vector of the α-atom. Eq. (2.1) gives a simple scheme for obtaining the crystal pseudopotential in real space for any crystal structure and material desired, provided one has a set of form factors $v_\alpha(G')$ and the lattice constant for the crystal of interest. A representative behavior of the real space pseudopotential $V_{\mathrm{p}}(r)$, reported previously[3] is shown in Fig. 1. Since $V_{\mathrm{p}}(r)$ reflects the valence electron distribution, the piling up of valence electrons between Ge (Ga, Zn, Cu) at $-d/8$ and Ge (As, Se, Br) at $d/8$ is evident. Here, d is the magnitude of the body diagonal in the zinc-blende structure. From Fig. 1, it is also noted that the potential well is displaced towards the electronegative element As (Se, Br). Moreover, the potential well becomes deeper as the compound increases its ionic character. Between Ge (Ga, Zn, Cu) at $d/8$ and Ge (As, Se, Br) at $7d/8$, a positive value of $V_{\mathrm{p}}(r)$ is observed, suggesting that the valence electrons will tend to avoid this region. The positive values of $V_{\mathrm{p}}(r)$ between $d/8$ and $7d/8$ can be understood by the presence of antibonding orbitals in this region. Conversely, the presence of bonding orbitals gives a minimum in the pseudopotential observed between $-d/8$ and $d/8$.[2],[3]

§3. Parameters of the dielectric theory of electronegativity

By analyzing the real space pseudopotentials used in previous studies,[2],[3] the following two relations have been found.

$$V_{\mathrm{p}}(r_c) = 2.59 E_{\mathrm{h}} + 0.95 \ , \tag{3.1}$$

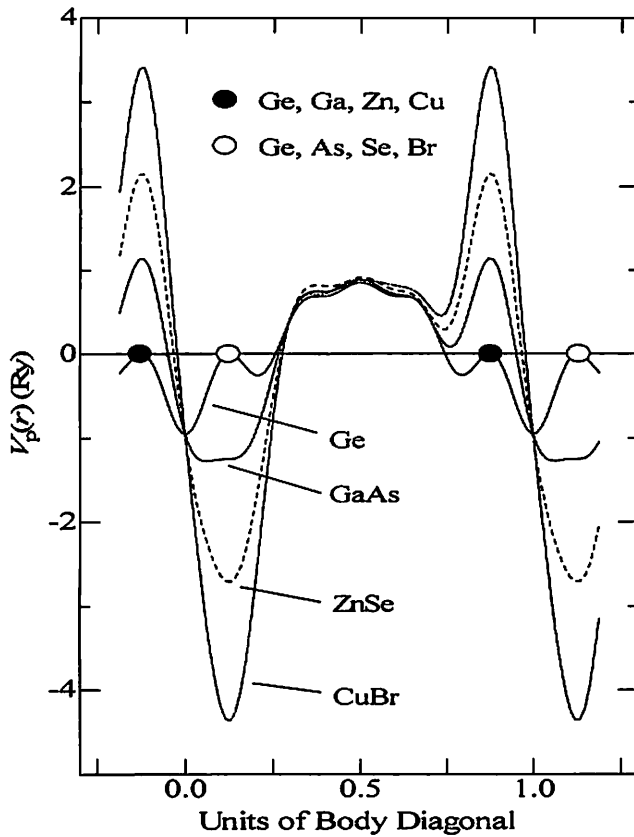$$V_{\mathrm{p}}(r_c)/V_{\mathrm{pm}} = -0.96 f_{\mathrm{i}} + 0.96 \ , \tag{3.2}$$

Fig. 1. Pseudopotential $V_p(r)$ along the [111] axis for Ge, GaAs, ZnSe and CuBr in the zinc-blende structure.

where $V_p(r_c)$ is the real space pseudopotential at mid point along the body diagonal in the zinc-blende structure, V_{pm} is the magnitude of the minimum value of the pseudopotential, E_h and f_i are the heteropolar gap and ionicity in the Phillips theory,[7] respectively.

Eq. (3.1) indicates that the values of the positive plateau observed in Fig. 1 are related with the homopolar gap. In other words, it is related with the symmetric part of the interatomic interactions.[20] The homopolar gap depends only on the bond length.[7] Since the bond length of the four compounds of Fig. 1 are almost the same,[21] the nearly constancy of $V_p(r)$ between $d/8$ and $7d/8$ observed in Fig. 1 is in harmony with the relation given in Eq. (3.1). The effects of bond length variation on the behavior of $V_p(r)$ has been studied previously.[22]

Eq. (3.2) gives the relation between the characteristics of the real space pseudopotential and the Phillips ionicity. A possible origin of the superionic behavior in AB type zinc-blende structure compounds has been discussed based on the quantities appearing in Eq. (3.2).[2),3),22]

Eqs. (3.1) and (3.2) give the average relation. It will be interesting to see to

Table I. Materials parameters used and calculated in the analysis. Real space pseudopotentials at mid point of the body diagonal in the zinc-blende structure, $V_p(r_c)$. Magnitude of the minimal value of the pseudopotential in real space, V_{pm}. Symmetrical part of the pseudopotential at $G = (2, 2, 0)$ in the reciprocal space, $V_s(220)$. Homopolar gap, E_h. Calculated f_i and Phillips f_i^{Ph} ionicity. Calculated Z_T and experimental Z_T^{Exp} transverse effective charge. The effective charges are normalized by the value of elementary charge.

Material	$V_p(r_c)$ (Ry)	V_{pm} (Ry)	$V_s(220)$ (Ry)	E_h (eV)	f_i	f_i^{Ph}	Z_T	Z_T^{Exp}
Si	0.991	1.030	0.054	4.77	0.013	0		
Ge	0.858	0.952	0.026	4.31	0.028	0		
Sn	0.463	0.701	0.012	3.06	0.033	0		
AlP	1.070	1.370	0.060	4.72	0.265	0.307	2.03	2.28
AlAs	0.930	1.352	0.039	4.38	0.305	0.274	1.94	2.30
AlSb	0.700	1.011	0.031	3.53	0.237	0.250	1.59	1.93
GaP	0.979	1.191	0.042	4.73	0.153	0.327	1.08	2.04
GaAs	0.890	1.272	0.024	4.32	0.271	0.310	1.54	2.16
GaSb	0.715	0.953	0.021	3.55	0.187	0.261	1.11	2.15
InP	0.749	1.239	0.018	3.93	0.314	0.421	1.69	2.55
InAs	0.701	1.594	0.005	3.67	0.499	0.357	2.27	2.53
InSb	0.667	1.050	0.010	3.08	0.351	0.321	1.78	2.42
ZnS	0.962	2.450	0.033	4.82	0.581	0.623	1.80	2.15
ZnSe	0.921	2.707	0.015	4.29	0.660	0.630	1.87	2.03
ZnTe	0.791	1.812	0.023	3.59	0.568	0.609	1.75	2.00
CdS	0.784	2.860	0.001	3.97	0.700	0.685	1.87	2.27
CdSe	0.713	3.087	-0.012	3.61	0.745	0.699	1.88	2.25
CdTe	0.709	2.171	0.002	3.08	0.686	0.717	1.84	2.35
CuCl	0.950	4.145	0.022	4.83	0.752	0.746	1.00	1.12
CuBr	0.888	4.372	0.005	4.14	0.796	0.735	1.00	1.49
CuI	0.822	2.975	0.024	3.66	0.732	0.692	1.00	2.40
AgI	0.706	3.439	-0.006	3.09	0.801	0.770	0.99	1.40

what extent these relations reproduce the parameters of the dielectric theory of electronegativity of a particular compound. Determination of such quantities from pseudopotentials will be also useful for the refinement of the pseudopotentials. It might also help to understand which part of the interatomic interactions contribute largely to the average bonding properties as incorporated in the Phillips theory.

From Eqs. (3.1) and (3.2), the ionicity f_i for several binary compounds with the zinc-blende structure has been calculated by using the values of $V_p(r_c)$ and V_{pm} as input parameters. One component materials are also considered for comparison. The result is given in Table I and Fig. 2. With the exception of few compounds, we can see that the agreement is quite well. In particular, it is gratifying to see the agreement in AgI and Cu halides, because the pseudopotentials for these compounds have been obtained by extrapolating the behavior of the pseudopotentials of other
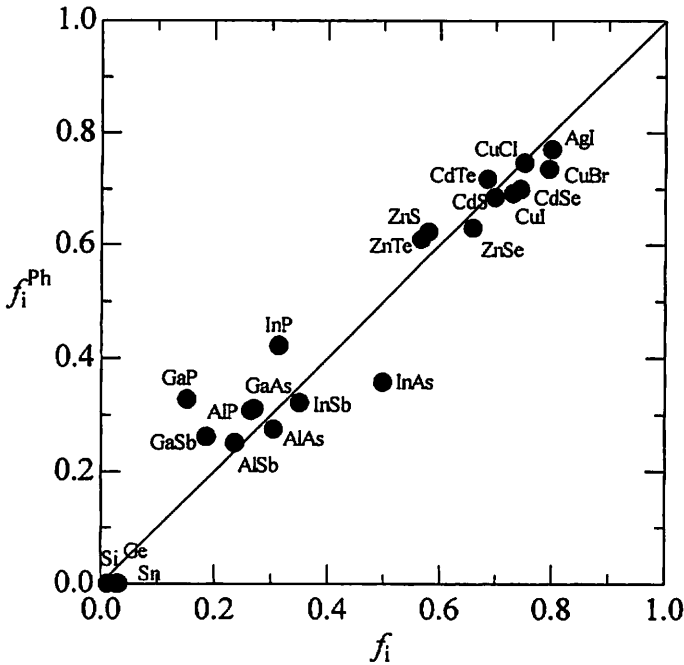
Fig. 2. Comparison between the calculated f_i and the Phillips f_i^{Ph} ionicity.

compounds.[22]

The Phillips ionicity is defined by[7]

$$f_i = \frac{C^2}{E_h^2 + C^2} ,$$ (3.3)

where C is the heteropolar gap. The values of C have been calculated from Eqs. (3.1) - (3.3) by using the pseudopotentials as input parameters. The result shown in Fig. 3 indicates that the agreement with the values given by Phillips is good. However, the degree of deviation is somewhat larger when compared with Fig. 2. Probably, this difference arises from the fact that the asymmetric part of the interatomic interaction is more subtle than the symmetric part.

§4. Transverse effective charge

An expression for the transverse effective charge that depends on the ionicity has been derived by Tomoyose.[23] It is given by

$$Z_T = \frac{\Delta Z}{2} + 4N_V \frac{(1-\delta)[f_i(1-f_i)]^{1/2}}{4(1-\delta)^2(1-f_i) + f_i} ,$$ (4.1)

where

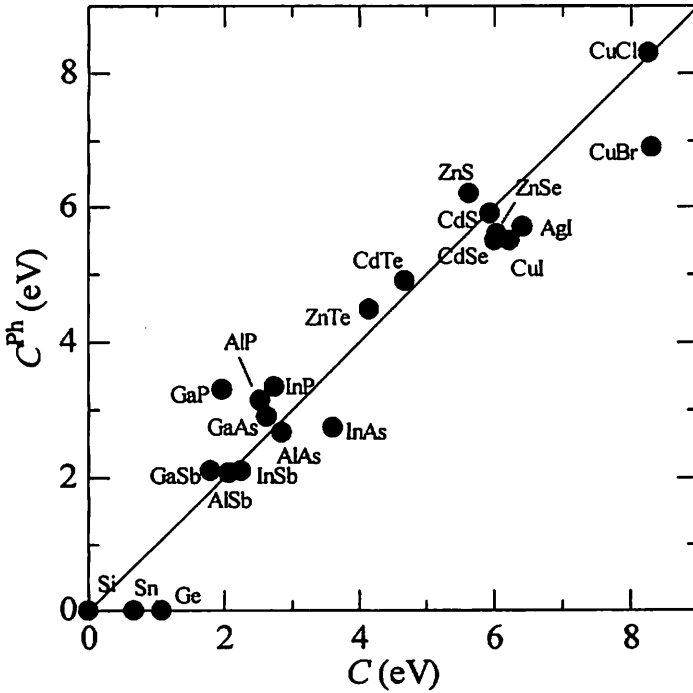$$\delta = \frac{2V_S(220)}{E_h} ,$$ (4.2)

Fig. 3. Comparison between the calculated C and Phillips C^{Ph} heteropolar gap.

and

$$\Delta Z = Z_{cation} + Z_{anion} \; . \qquad\qquad (4.3)$$

In the above expressions, ΔZ is the difference of the valence between cations and anions. $N_V = 4$ is the number of valence electrons per atom. $V_S(220)$ is the value of the pseudopotential at $G = (2,2,0)$ in the reciprocal space.

The values of Z_T have been calculated by using the ionicity determined in the previous section. The values of $V_S(200)$ are given in Table I. For the values of Z_{cation} and Z_{anion}, nominal values for III-V, II-VI and I-VII compounds are used. The results of the calculations are shown in Table I and Fig. 4. We can see that the agreement is not good. The calculated values are systematically smaller than the experimental values.[24),25)] Moreover, we can not see any chemical trend in the calculated values. This discrepancy may be due to several factors. The first is the use of nominal values for the valence. Concerning this point, Wakamura[26)] has suggested that the valence in certain compounds is shifted systematically. The second factor is the use of $N_V = 4$ for the number of valence electrons per atom. For the case of superionic materials, it has been suggested that the effective number of valence electrons might differ from the usual 8 electrons per atom pair rule, due to the contribution of d-electrons.[27)] The discrepancies observed for AgI and Cu halides may be largely due to these two factors. The third factor is the approximation used in the derivation of Z_T. The fourth factor arises possibly from the inadequacy of the pseudopotential used. Inspection of Figs. 2 - 4, suggests that the pseudopotentials of some compounds
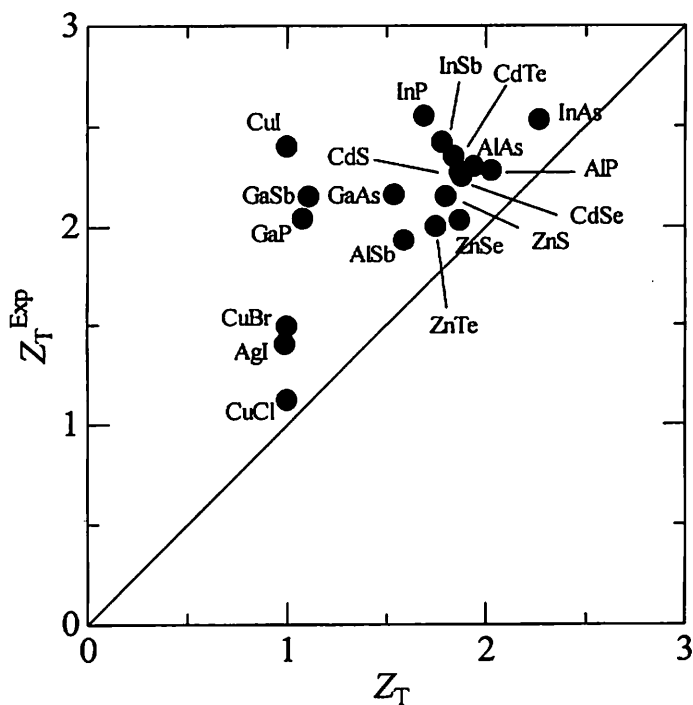
Fig. 4. Comparison between the calculated Z_T and the experimental Z_T^{Exp} values of the transverse effective charge. The effective charges are normalized by the value of elementary charge.

such as GaP need reconsideration.

§5. Conclusion

The analyses presented in previous sections indicate that the pseudopotentials used in the previous studies are in general consistent with the dielectric theory of electronegativity, although some refinements are required. Concerning the transverse effective charge, the analysis suggests the importance of the quantities such as effective valence and effective number of valence electrons.

Acknowledgements

References

1) M.L.Cohen, Ann.Rev.Mater.Sci. **14** (1984), 119.
2) M.Aniya, Solid State Ionics **70-71** (1994), 673.
3) M.Aniya, J.Phys.Chem.Solids **57** (1996), 1811.
4) M.O'Keeffe, Comments Solid State Phys. **7** (1977), 163.
5) H.Hayashi, M.Kobayashi and I.Yokota, Solid State Commun. **31** (1979), 847.
6) F.Shimojo, M.Aniya and K.Hoshino, J.Phys.Soc.Jpn. **73** (2004), 2148.

7) J.C.Phillips, Rev.Mod.Phys. **42** (1970), 317.
8) J.A.Van Vechten, Phys.Rev. **182** (1969), 891.
9) N.Kuroda and Y.Nishina, J.Phys.Soc.Jpn. **50** (1981), 2969.
10) A.Yoshiasa, K.Koto, H.Maeda and T.Ishii, Jpn.J.Appl.Phys. **36** (1977), 781.
11) M.Aniya, Phys.Rep.Kumamoto Univ. **10** (1998), 161.
12) T.Tomoyose, Solid State Ionics **79** (1995), 13.
13) M.Aniya and K.Wakamura, Physica B **219&220** (1996), 463.
14) M.Aniya and K.Wakamura, Solid State Ionics **86-88** (1996), 183.
15) T.Tomoyose, A.Fukuchi and M.Aniya, J.Phys.Soc.Jpn. **65** (1996), 3692.
16) K.Wakamura, J.Phys.Chem.Solids **59** (1998), 591.
17) M.Aniya, Solid State Ionics **121** (1999), 281.
18) F.Aymerich, F.Meloni and G.Mula, Phys.Rev. **B15** (1977), 3980.
19) Y.W.Tsang and M.L.Cohen, Phys.Rev. **B9** (1974), 3541.
20) J.C.Phillips, in *Handbook on Semiconductors*, Ed. T.S.Moss (Elsevier, Amsterdam, 1992), Vol.1, p.47.
21) W.A.Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
22) M.Aniya, J.Phys.Soc.Jpn. **61** (1992), 4474.
23) T.Tomoyose, J.Phys.Soc.Jpn. **63** (1994), 2085.
24) G.Lucovsky, R.M.Martin and E.Burstein, Phys.Rev. **B4** (1971), 1367.
25) S.Katayama and H.Kawamura, Solid State Commun. **21** (1977), 521.
26) K.Wakamura, Solid State Commun. **86** (1993), 503.
27) M.Aniya and K.Wakamura, in *Solid State Ionics: Science & Technology*, Ed. B.V.R.Chowdari *et al.* (World Scientific, Singapore, 1998), p.43.