Analysis of the Bond Ionicity in Solids: Searching a Guideline for the Design of New Superionic Conducting Materials

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The bond ionicity of a binary compound is analyzed by using the dielectric theory of electronegativity and the bond orbital model. The effect of varying the number of valence electrons, the bond length, and the interatomic interaction parameter is studied. By connecting the result of the analysis with the bond fluctuation model of superionic conductors suggested by the author, possible guidelines for the development of new superionic conducting materials is discussed.

§1. Introduction

Among the various classes of substances, there is a class of solid materials called superionic conductors. These materials are characterized by their high ionic conductivities with an order of magnitude as is usually found in molten salts. There, the high ionic conductivity is due to the movement of one kind of ion between·sites provided by the immobile ion sublattice. The reason that these materials can exhibit such high ionic conductivities has been traditionally understood from the point of view of materials structure.[1),2)] Surely structure is an important factor that determines the fast ion transport within the solid. But it is not the only factor. In order to answer to a question such as why only a certain class of materials can behave as superionic conductors, it is necessary to take into account also the electronic structure of the materials. Recent studies have revealed that superionic conduction is closely related to the bonding characteristics of the materials.[3)−12)] Concerning the origin of superionic properties, the author has suggested that a change of bonding which occurs locally and fluctuates in time plays an important role.[4)−7)] There it is considered that local fluctuations of the bonding creates a field of forces which move the ions, which in turn triggers new bond fluctuations. The mechanism of bond fluctuation in superionic conductors has been used successfully in the interpretation of experimental observations.[13)−17)] Theoretical studies based on a pseudopotential method also support the view that bond fluctuations may occur in superionic conductors.[5),6),18)] A simple phenomenological formulation of bond fluctuation in superionic conductors has been given by exploiting the analogies with the phenomenon of chemical equilibria.[19)]

Generally speaking, the properties of the materials are intimately related with their bonding nature. A well succeeded theory for the study of bonding in solids is the dielectric theory of electronegativity developed by Phillips and Van Vechten.[20),21)] The concept of crystal ionicity introduced there has been used in a wide variety of areas such as relation between crystal structure and band structure, elastic constants,

piezoelectric constants, cohesive energies, impurity binding energies, etc. Another theory well succeeded in the study of bonding properties of solids is the bond orbital model developed by Harrison and co-workers.[22]

In the present report, the effect of varying the number of valence electrons, the interatomic distance and the interatomic interaction parameters on the bond ionicity of a binary compound is analyzed by using the Phillips - Van Vechten theory and the bond orbital model. By connecting the result of the analysis with the mechanism of superionic transport suggested by the author, possible guidelines for designing new superionic conducting materials are discussed.

§2. Bond fluctuation model of superionic conductors

Consider a solid material in which the ions are vibrating around their lattice sites. As the position of the ion core moves, the electrons follow this movement and a deformation of the electronic cloud distribution takes place. On the other hand, the deformed electronic cloud creates a new field of forces to move the ions. Within this picture of ion dynamics, the characteristic of superionic conductors resides in the fact that the electronic cloud deformation is easily induced. That is, a small disturbance in the electronic subsystem leads to a drastic change in the local structure of the ionic subsystem and vice versa. In previous reports,[4]−[7),19] this idea has been described as a local fluctuation of the chemical bond which occurs within a superionic solid. The summary of the idea is illustrated in Fig. 1.
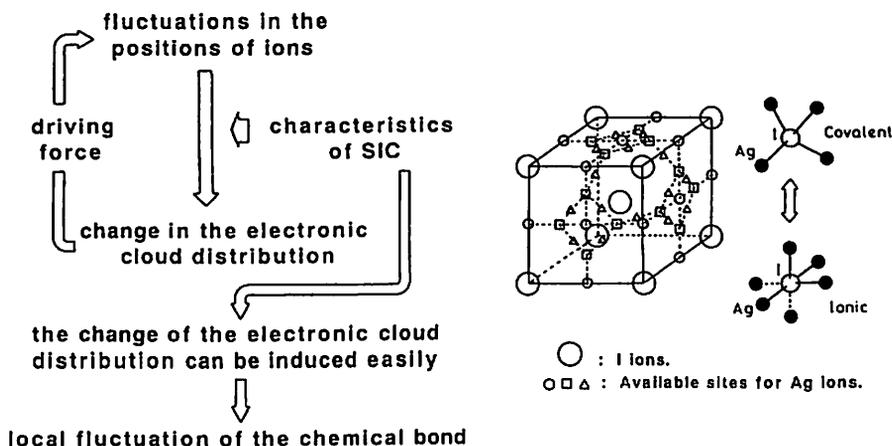

Fig. 1. Schematic representation of the concept of bond fluctuation in superionic conductors. The figure on the right hand side illustrates the case for AgI.

Phenomenologically, the bond fluctuations can be described as follows.[19] Let us denote by A and B the stable and metastable local bonding configurations, respectively. The sites B are the sites where bond fluctuations have occurred. At a given thermodynamical state, the bond fluctuations considered is described phenomeno-

logically as $A \rightleftharpoons B$. Denoting by $[A]$ and $[B]$ the concentrations of A and B, and assuming that $[A] + [B] = 1$, the rate of bond fluctuations is given by[19]

$$d[B]/dt = k(1 - [B])\exp(-\Delta G^*/RT) - k[B]\exp\{-(\Delta G^* - \Delta G^0)/RT\}$$
$$= k\exp(-\Delta G^*/RT)\{1 - [B](1 + \exp(\Delta G^0/RT))\}, \qquad (2.1)$$

where k is the proportionality coefficient, R is the gas constant and T is the temperature. ΔG and ΔG^0 are the Gibbs free energies as specified in Fig. 2. In equilibrium we have $d[B]/dt = 0$, therefore

$$[B]_\infty = [1 + \exp(\Delta G^0/RT)]^{-1}. \qquad (2.2)$$

Eq. (2.2) gives the average concentration of sites in the configuration B at a given thermodynamical state. The behavior of eq. (2.2) is illustrated in Fig. 3. Note that, in the low temperature region, $[B]_\infty$ is practically equal to zero. This means that at such temperatures there are no bond fluctuations.
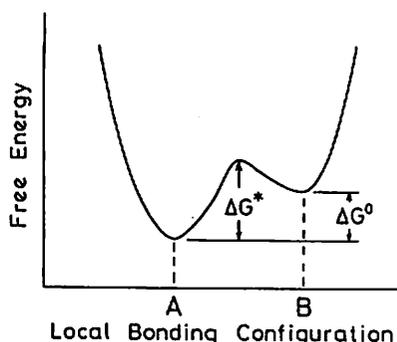

Fig. 2. Diagram illustrating the energy profile as a fuction of local bonding configuration.

Making connection with the structure, the fluctuation of the chemical bond is reflected in the local coordination number at a particular moment. For instance, in the superionic conducting materials such as AgI and Cu halides, the mobile ion species (Ag and Cu, respectively) are surrounded by 4 anions in the low temperature non-superionic phase. In the superionic phase, the mobile ion takes instantaneously, a different coordination number from 4 as it moves between sites provided by the cage ion sublattice. Many studies have revealed that among a wide variety of possible paths, an important path of the mobile ion is through the tetrahedral $\rightarrow$ octahedral $\rightarrow$ tetrahedral site occupation.[23),24)] That is, an important type of local bond fluctuation that occurs accompanying the mobile ion dynamics is covalent $\rightarrow$ ionic $\rightarrow$ covalent bond fluctuations.[4)-7)]

Evidence for the fluctuation of the chemical bond has been investigated by measuring the temperature dependence of the dynamical effective charge in AgI[15)] and Ag_3SI.[16)] The behavior for the case of AgI is shown in Fig. 4. The effective charge in the low temperature non-superionic phase, decreases with the increase of temperature. This behavior has been observed also in the non-superionic phases of
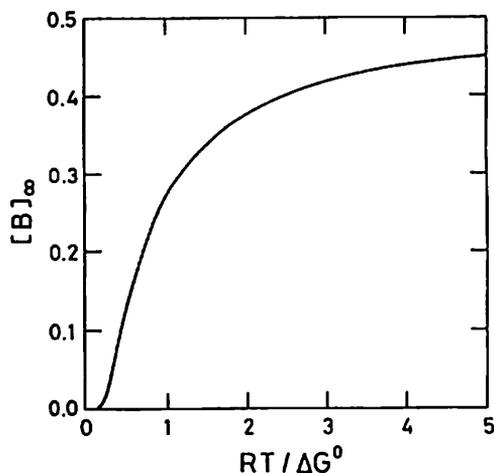
Fig. 3. Temperature dependence of the equilibrium concentration of sites with the local bonding configuration denoted as B in Fig. 2.
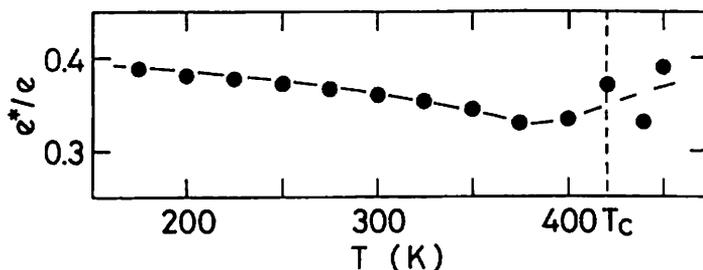

Fig. 4. Temperature dependence of the effective charge in AgI.

Ag_3SI[16] and CuI.[25] On the other hand, in the high temperature superionic phase, the effective charge increases with temperature.[15],[16] It is known that the dynamical effective charge in a typical semiconductor and ionic crystal decreases with the increase of temperature.[26] Therefore, the temperature dependence of the dynamical effective charge in the superionic phase is anomalous. The origin of the anomaly is explained if in the superionic phase the ionic bonded sites have emerged as fluctuations as mentioned above. Since the magnitude of the effective charge correlates with the magnitude of the ionicity, the behavior of the effective charge[15],[16] indicates that the ionicity of the compound has increased in the superionic phase. Moreover, comparative studies of bonding in various compounds by using a pseudopotential method, support the view that an ionic bonded site is induced more easily in superionic compounds such as AgI and Cu halides than in non-superionic compounds such as GaAs, InSb, ZnSe, etc.[5],[6),[18] Interesting behavior of the pressure dependence of the effective charge[27] and related property[28] have been also reported.

§3. Effective number of valence electrons

Many studies have revealed that in AgI and Cu halides, the d-electrons are contributing to the bonding.[3),4),8),12),29),30)] The contribution of d-electrons is expected to be important in the stabilization of the 4-fold coordination of these compounds.[4)] However, since d-electrons are more localized than s- and p-electrons, its ability to form a bonding orbital is weak. The bond fluctuation model states that these weak bonds are forming and destroying accompanying the lattice vibrations.[4)−7)] Then, as the temperature is increased and the atomic vibration becomes more disordered, the contribution of d-electrons to the bonding decreases in average. That is, the effective number of valence electrons in superionic compounds is expected to decrease with the increase of temperature. The temperature dependence of the effective number of valence electrons, Z in AgI has been determined by using a plasma oscillation theory of solids.[31)] The result is shown in Fig. 5.[32)] We note that the value of Z is smaller than 8, the value expected when the halogen and silver contribute with 7 and 1 valence electrons, respectively. This discrepancy between the obtained and the expected values is due to the use of a rough theory. The temperature dependence of Fig. 5 shows however, the behavior predicted by the bond fluctuation model of superionic conductors as discussed above.
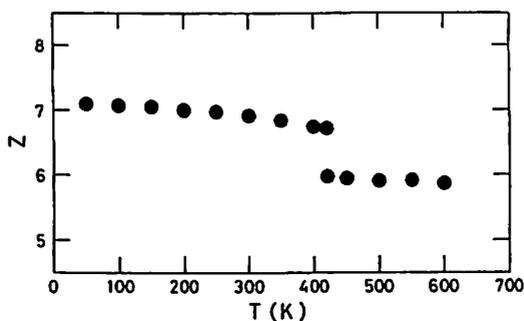

Fig. 5. Temperature dependence of the effective number of valence electrons in AgI.

By comparing Figs. 4 and 5, the following scenario of the bonding can be drawn. Although not apparent from Fig. 5, the effective number of valence electrons in the low temperature phase should be larger than 8 due to the contribution of d-electrons,[4),8),30)] and the dominant type of bonding is covalent.[4)] As the temperature is increased, the bond fluctuation occurs by breaking the bond due to d-electrons. That is, the ionic bonded sites are induced locally and the effective number of valence electrons approaches to $Z = 8$. This is manifested in the local change of the coordination number and in the increase of the effective charge.[15),16)]

The ionicity of the crystal is a useful quantity to characterize the bonding nature.[20)] In the following, the effect of varying the bond length and the number of valence electrons on the crystal ionicity is analyzed. The ionicity of a compound $A_m B_n$ is given by[20),21),33)]

$$f = C^2/(E_h^2 + C^2), \tag{3.1}$$

$$E_h = 39.74/d^{2.48} \quad \text{eV}, \tag{3.2}$$

$$C = 14.4b[Z_A/r_0 - (n/m)Z_B/r_0]\exp(-k_s r_0) \quad \text{eV}, \tag{3.3}$$

$$r_0 = d/2, \tag{3.4}$$

$$b = 0.089N_c^2, \tag{3.5}$$

$$k_s = (4k_F/\pi a_0)^{1/2} = 2.262(N_F^{1/3}/d)^{1/2} \quad \text{Å}^{-1}, \tag{3.6}$$

where f is the ionicity, E_h and C are the homopolar and heteropolar gaps, respectively. d is the nearest-neighbor distance, $Z_A(Z_B)$ is the number of valence electrons of the cation (anion) per formula unit.
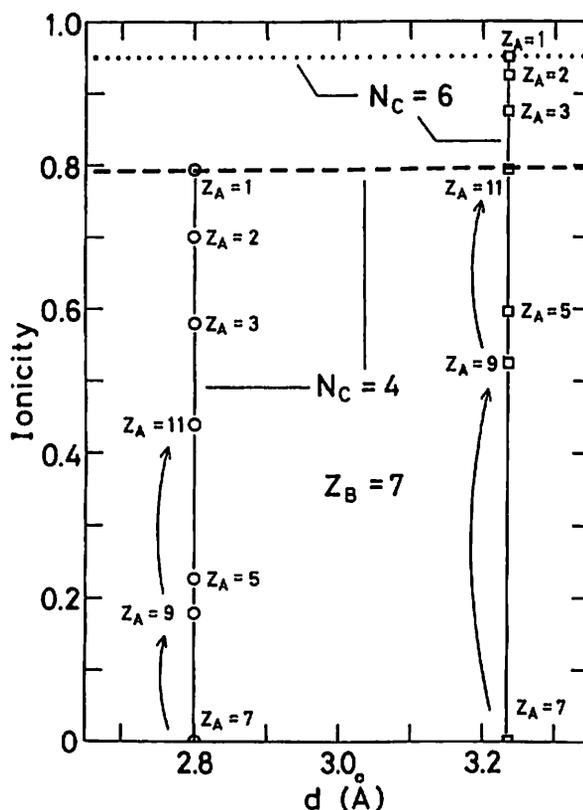

Fig. 6. Bond ionicity as a function of bond length and number of valence electrons. The cases for 4-fold and 6-fold coordination are shown.

The result of the analysis is summarized in Fig. 6. First of all, we note that the 6-fold coordination compound is more ionic than the 4-fold coordination compound.[20]

In both cases, the bond ionicity is practically insensitive to the variation of inter-atomic distance. This behavior is rather strange, because the bond ionicity is expected to change appreciably by the application of pressure.[4],[34] Fig. 6 shows also the effect of varying the number of valence electrons. It shows that the bond ionicity decreases by increasing the number of valence electrons, that is the contribution of d-electrons. When $Z_A = Z_B = 7$, the compound becomes completely covalent and for $Z_A > 7$, the bond ionicity increases again.

§4. Interatomic interaction parameter and ionicity

An empirical correlation between the bond ionicity and the band parameters given by

$$f = 0.5[1 - \cos(\pi E_{AS}/E_{VB})], \tag{4.1}$$

has been found by Unger and Neumann.[35] Here E_{AS} is the antisymmetric gap and E_{VB} is the total valence band width. In the bond orbital model, for the tetrahedral solids these band parameters are given by[22],[36]

$$E_{VB} = \Delta\Gamma = 4(V_1^S + 2V_1^x) + 4[\alpha_p V_1^A - 2(1 - \alpha_c)V_1^x], \tag{4.2}$$

$$E_{AS} = \Delta X = 4V_1^A + 4\alpha_p V_1^S. \tag{4.3}$$

The quantities V_1^S and V_1^A are written in terms of the atomic parameters as

$$V_1^S = (V_1^a + V_1^c)/2, \tag{4.4}$$

$$V_1^A = (V_1^a - V_1^c)/2, \tag{4.5}$$

$$V_1^a = (\varepsilon_p^a - \varepsilon_s^a)/4, \tag{4.6}$$

$$V_1^c = (\varepsilon_p^c - \varepsilon_s^c)/4, \tag{4.7}$$

where $\varepsilon_s^a(\varepsilon_s^c)$ and $\varepsilon_p^a(\varepsilon_p^c)$ are the energies of the s- and p-electrons of the anion (cation) as shown in Fig. 7. The polarity α_p and the covalency α_c are given by

$$\alpha_p = V_3/(V_2^2 + V_3^2)^{1/2}, \tag{4.8}$$

$$\alpha_c = V_2/(V_2^2 + V_3^2)^{1/2}, \tag{4.9}$$

where

$$V_3 = (\varepsilon^c - \varepsilon^a)/2, \tag{4.10}$$

$$\varepsilon^c = (\varepsilon_s^c + 3\varepsilon_p^c)/4, \tag{4.11}$$

$$\varepsilon^a = (\varepsilon_s^a + 3\varepsilon_p^a)/4. \tag{4.12}$$

The quantities V_1^x and V_2 are written in terms of the universal tight-binding parameters as
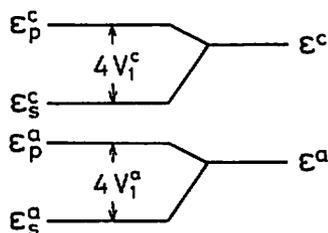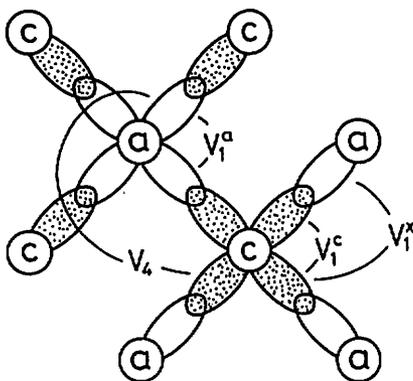
Fig. 7. Energy diagram.

Fig. 8. Interaction parameters of the bond orbital model used in this report.

$$V_1^x = -(A_{ss} + 2\sqrt{3}A_{sp}/3 - A_{pp})/4 = 5.03/d^2 \quad \text{eV Å}^2, \qquad (4.13)$$

$$V_2 = -(A_{ss} + 2\sqrt{3}A_{sp} + 3A_{pp})/4 = 33.30/d^2 \quad \text{eV Å}^2, \qquad (4.14)$$

where d is the bond length. The meaning of the interaction parameters used here is illustrated in Fig. 8. The role playing by these parameters in the determination of the band structure of a tetrahedral solid is shown in Fig. 9. Note that the antisymmetric gap is determined by V_1^a and V_1^c. On the other hand, the total valence band width is determined by V_1^x. Therefore, from eq. (4.1), we can say that the bond ionicity is characterized mainly by these three parameters.

In Fig. 10, the bond length dependence of $\Delta\Gamma$, ΔX and the ionicity is shown. In the evaluation, the material parameters for AgI have been used. Namely, $\varepsilon_s^c = -6.41$ eV, $\varepsilon_p^c = -2.05$ eV, $\varepsilon_s^a = -19.42$ eV and $\varepsilon_p^a = -9.97$ eV.[22] It is shown that the ionicity decreases with the decrease of bond length. This behavior is consistent with the results of high pressure experiments done in some non-superionic materials.[34] However, it seems to be inconsistent with the behavior expected in superionic materials.[4]
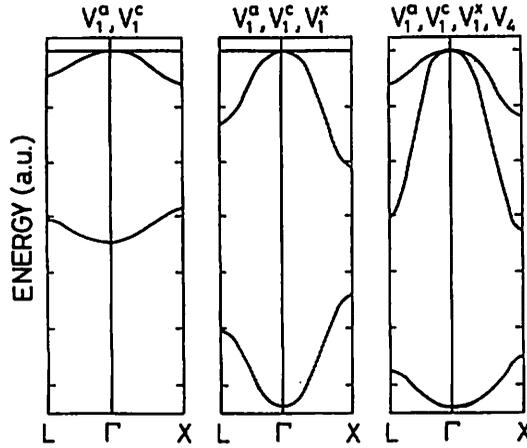
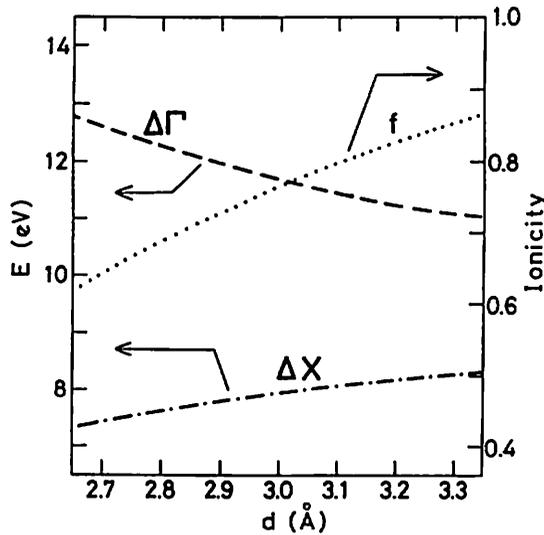Fig. 9. Effect of the interaction parameter on the valence band.[22),36)]

Fig. 10. Bond-length dependence of the total valence band width $\Delta\Gamma$, antisymmetric gap ΔX and ionicity.

The value of the ionicity can be modified by changing the values of V_1^a, V_1^c and V_1^x. The values of the parameters V_1^a and V_1^c are determined by the species of the atoms. In order to see the effect of V_1^x, the following operation has been done

$$V_1^x \rightarrow \beta V_1^x, \qquad (4.15)$$

where β is a numerical factor varying between 0 and 1. The behavior for the case

of AgI, with $d = 2.8$ Å is shown in Fig. 11. It is seen that the ionicity increases by diminishing the value of the parameter V_1^x. This behavior is consistent with the trend of melting temperature in diverse materials reported previously.[37]
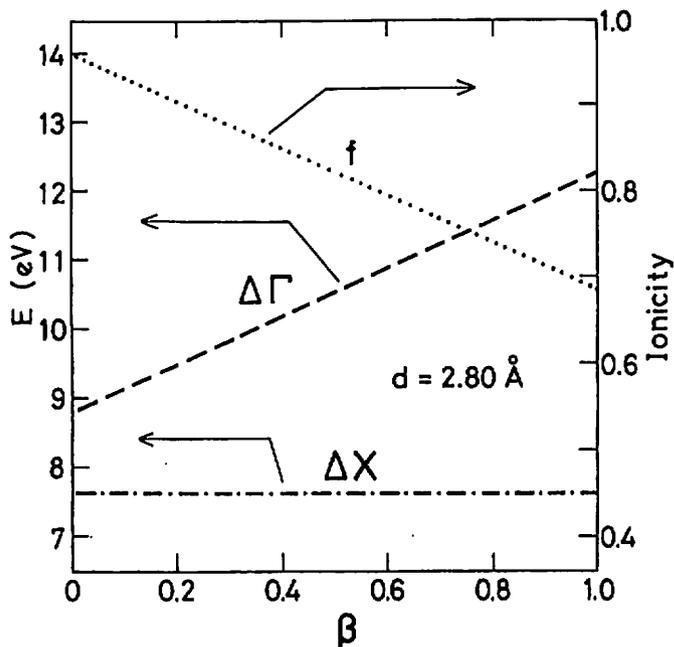

Fig. 11. Dependence of the total valence band width $\Delta\Gamma$, antisymmetric gap ΔX and ionicity on the interaction parameter written as βV_1^x.

§5. Conclusion

In the present report, the bond ionicity of a binary compound has been analyzed by using the dielectric theory of electronegativity[20],[21] and the bond orbital model.[22],[36] The effect of varying the number of valence electrons, the bond length and the interatomic interactions on the bond ionicity have been studied. The result of the analysis have been correlated with the bond fluctuation model of superionic conductors.[4]−[7],[19] Some of the results were in agreement, whereas others disagreed. The origin of the disagreement may be due to the inadequacy of the theories in dealing superionic materials. This is not so surprising, because in these theories the contribution of d-electrons are not taken into account. Alternatively, the disagreement may be an indication that the bond fluctuation model is requiring a revision. Further study is necessary to clarify this point.

However, the increase of the ionicity in the superionic phase seems to be a notable characteristic.[15],[16] Therefore, a possible guideline for the development of new

superionic conductors is to search a 4-fold coordinated compound[4] whose ionicity increases easily under some external force or chemical substitution.

Acknowledgements

References

1) S. Hoshino, Solid State Ionics **48** (1991), 179.
2) T. Sakuma, Bull. Electrochem. **11** (1995), 57.
3) H. Takahashi, S. Tamaki and Y. Waseda, Solid State Ionics **31** (1988), 55.
4) M. Aniya, Solid State Ionics **50** (1992), 125.
5) M. Aniya, J. Phys. Soc. Jpn. **61** (1992), 4474.
6) M. Aniya, Solid State Ionics **70/71** (1994), 673.
7) M. Aniya, in *Solid State Ionic Materials*, ed. B. V. R. Chowdari et al. (World Scientific, Singapore, 1994), p. 223.
8) K. Wakamura, Solid State Commun. **82** (1992), 705.
9) B. J. Wuensch, Mater. Sci. Eng. B **18** (1993), 186.
10) T. Yamanishi, T. Kanashiro, Y. Michihiro, Y. Kishimoto and T. Ohno, J. Phys. Soc. Jpn. **64** (1995), 643.
11) T. Tomoyose, Solid State Ionics **79** (1995), 13.
12) A. Rakitin and M. Kobayashi, Phys. Rev. **B53** (1996), 3088.
13) M. Aniya, Solid State Ionics **79** (1995), 259.
14) M. Aniya, J. Non-Cryst. Solids **198-200** (1996), 762.
15) M. Aniya and K. Wakamura, Physica B **219&220** (1996), 463.
16) M. Aniya and K. Wakamura, Solid State Ionics **86-88** (1996), 183.
17) J. Kawamura, Nihon Gakujutsu Shinkokai, Amorphous - Nano Zairyo Iinkai 147-56 (1997), 13.
18) M. Aniya, J. Phys. Chem. Solids **57** (1996), 1811.
19) M. Aniya, J. Phys. Soc. Jpn. **65** (1996), 3406.
20) J. C. Phillips, Rev. Mod. Phys. **42** (1970), 317.
21) J. A. Van Vechten, Phys. Rev. **182** (1969), 891.
22) W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
23) P. Vashishta and A. Rahman, Phys. Rev. Lett. **40** (1978), 1337.
24) M. Kobayashi, K. Ishikawa, F. Tachibana and H. Okazaki, Phys. Rev. **B38** (1988), 3050.
25) M. Aniya, Mem. Fac. Gen. Educ., Kumamoto Univ., Nat. Sci. **31** (1996), 17.
26) K. Wakamura, J. Phys. Chem. Solids **54** (1993), 387.
27) M. Aniya, Ext. Abstr., 21th Symp. Solid State Ionics in Japan (1995), 27.
28) M. Aniya, T. Tomoyose and M. Kobayashi, Phys. Stat. Solidi (b) **196** (1996), K17.
29) A. Goldmann, Phys. Stat. Solidi (b) **81** (1977), 9.
30) T. Tomoyose, A. Fukuchi and M. Aniya, J. Phys. Soc. Jpn. **65** (1996), 3692.
31) V. K. Srivastava, Phys. Stat. Solidi (b) **114** (1982), 667.
32) M. Aniya and K. Wakamura, Submitted for publication.
33) B. F. Levine, Phys. Rev. **B7** (1973), 2591.
34) B. Okai, *Kagaku Sosetsu* No.22 (1979), 119.
35) K. Unger and H. Neumann, Phys. Stat. Solidi (b) **64** (1974), 117.
36) S. T. Pantelides and W. A. Harrison, Phys. Rev. **B11** (1975), 3006.
37) M. Aniya, J. Chem. Phys. **96** (1992), 2054.