Madelung Energy of the Valence Skipping Compound BaBiO$_3$

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Several elements show valence skip fluctuation, for instance, Tl forms the compounds in valence states +1 and +3, Bi and Sb form with +3 and +5 states, and Pb and Sn with +2 and +4 valence states. It is reasonable to expect a new microscopic physics behind this phenomenon. The reason for the missing of some valence states in such valence skip compounds remains a mystery. We have performed the evaluation of the Madelung potential for BaBiO$_3$, and have shown for the first time that charge-ordered state is stabilized if we take into account the polarization of the oxygen charge. We argue that the effective Coulomb interaction energy $U$ may be negative evaluating the local excitation energy.

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In the periodic table more than ten elements show valence skip in all the compounds they form. Ti and In form the compounds with the valence states +1 and +3, Bi and Sb form with +3 and +5 states, and Pb and Sn with +2 and +4 valence states. It is reasonable to expect a new microscopic physics behind this phenomenon. The reason for missing valence states for these elements still remains a mystery[1, 2, 3]. The valence skipping leads to the Hubbard type model with the negative-U attractive interaction. Since the attractive interaction possibly promotes superconductivity, the carrier doping may induce superconductivity with relatively high $T_c$. For example, Ba$_{1-x}$K$_x$BiO$_3$ shows high $T_c$ which is unlikely from the conventional electron-phonon mechanism. The reason for the missing of some valence states in such valence skip compounds remains a mystery. We have performed the evaluation of the Madelung potential for BaBiO$_3$, and have shown for the first time that charge-ordered state is stabilized if we take into account the polarization of the oxygen charge. We argue that the effective Coulomb interaction energy $U$ may be negative evaluating the local excitation energy.

The valence skip is important in the study of a charge Kondo effect[15] as well as valence-fluctuation induced superconductivity[16]. A superconductor Pb$_{1-x}$Tl$_x$Te with $T_c = 1.4K[17]$ is reasonably expected to belong to the same category. The mother compound PbTe is a small gap semiconductor. For Tl concentrations up to the solubility limit 1.5 percent, the material shows superconductivity with a remarkably high $T_c$ as a low carrier metal. Tl impurities as negative-U centers could leads to superconductivity and at the same time Kondo effect as a charge analog[13, 15].

The purpose of this paper is to investigate the mystery of missing valence states evaluating the intra-atomic energy for Bi$^{4+}$ ion. In general, the total energy is the sum of the one-body potential energy and the interaction energy. The Coulomb interaction is primarily important for the insulator BaBiO$_3$. The curvature of the total energy as a function of the valence $n$, which is closely related with the intra-atomic energy $U$, may be presumably changed due to the Coulomb interaction. In the way stated we calculate the Madelung energy of BaBiO$_3$. Let $q_i$ be the charge on the site $i$, the total Coulomb energy is

$$E = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{r_{ij}}, \quad (1)$$

where $r_{ij}$ is the distance between the sites $i$ and $j$. If we define the potential at the site $i$ as

$$V_i = \sum_{j \neq i} \frac{q_j}{r_{ij}}, \quad (2)$$

the total Coulomb energy is

$$E = \frac{1}{2} \sum_i q_i V_i. \quad (3)$$

The potential $V_i$, called the Madelung potential, is evaluated using the Ewald method[19, 20]. We calculated
the Madelung potential and the total energy for the valence skipping compound BaBiO$_3$. We assign the formal charges as

(A) Ba : 2+, Bi : 4+, O : 2–

(B) Ba : 2+, Bi(1) : 3+, Bi(2) : 5+, O : 2–

where in the latter case the charge density wave with valences 3+ and 5+ is assumed. Let us denote the number of Ba atoms as $N_A$, then the number of Bi and O atoms are $N_A$ and $3N_A$, respectively. The total Madelung energy for the case (A) is

$$E_{Madel} = \frac{1}{2}(N_{aqBa}V_{Ba} + N_{aqBi}V_{Bi} + 3N_{aqO}V_O)$$

$$= \frac{N_A}{2}(q_{Ba}V_{Ba} + q_{Bi}V_{Bi} + 3q_{O}V_O),$$

where $q_{Ba} = 2$, $q_{Bi} = 4$ and $q_{O} = -2$. For the case (B) the total Madelung energy is

$$E_{Madel} = \frac{N_A}{2}(q_{Ba}V_{Ba} + \frac{1}{2}q_{Bi(1)}V_{Bi(1)} + \frac{1}{2}q_{Bi(2)}V_{Bi(2)} + 3q_{O}V_O),$$

for $q_{Ba} = 2$, $q_{Bi(1)} = 3$, $q_{Bi(2)} = 5$ and $q_{O} = -2$. The intra-atomic repulsion energy $U$ can be calculated if the total energy is obtained. For the valence $n$, the energy $U$ is defined as

$$U_n = E_{n+1} + E_{n-1} - 2E_n,$$

where $E_i$ is the energy of the valence $i$ state. The $U$ for Bi$^{4+}$ per two bismuth atoms has been estimated from the measured ionization energies of the elements as

$$U_{4+} = E_{ion}(Bi^{3+}) + E_{ion}(Bi^{5+}) - 2E_{ion}(Bi^{4+}) = 10.7eV.$$

Here $E_{ion}(Bi^{n+})$ is the ionization energy of the element Bi$^{n+}$. This estimated value is quite large although it is smaller than for Bi$^{3+}$ ($U_{3+} = 19.7eV$) and Bi$^{5+}$ ($U_{5+} = 32.3eV$). Thus the simple estimate results in the positive $U$.

We compare the total energy of the uniform state (A) and the ordered CDW state (B), where the total energy is the sum of the total Madelung energy and the one-body (ionic) potential energy. The total energy difference is

$$\Delta E = E(Ba_2^{2+}Bi^{3+}Bi^{5+}O_6^{2–}) - E(Ba_2^{2+}Bi^{4+}Bi^{4+}O_6^{2–})$$

$$+ E_{ion}(Bi^{5+}) + E_{ion}(Bi^{3+}) - 2E_{ion}(Bi^{4+}),$$

where $E(Ba_2^{2+}Bi^{3+}Bi^{5+}O_6^{2–})$ and $E(Ba_2^{2+}Bi^{4+}Bi^{4+}O_6^{2–})$ are the total Madelung energies per two BaBiO$_3$’s, respectively. The charge-ordered state is stabilized if $\Delta E$ is negative. The Madelung potential $V_a$ ($a=\text{Ba, Bi and O}$) are shown in the Table I where we use the convention that the potential $V_i$ is negative for the positive charge $q_i > 0$. The total potential energy per BaBiO$_3$, $E_{tot}/N_A$, is -81.95 eV for (A) and -83.40 eV for (B), respectively, which are shown in the first and second rows of the Table I. Apparently the case (B) with the charge density wave has the lower energy. From these values, we obtain $\Delta E = 7.8eV$ which is still positive. It is now important to notice that the $\Delta E$ is reduced if we consider the movement of the oxygen ions. The neutron diffraction demonstrated that the Bi ions occupy two crystallographically inequivalent sites with different Bi-O bond lengths.$^{[5]}$ It has been reported by the neutron diffraction experiment that the oxygen atoms are out of the center of two Bi ions by 4 percent of the Bi-O bond length due to lattice relaxation$^{[10]}$ (see Fig.1). Thus it is reasonable to move the positions of oxygen atoms with different Bi-O bond lengths in calculating the Madelung potential. In order to take into account the polarization of electrons of oxygen atoms, we have further moved the center of point charges more than reported by the neutron diffraction. It is plausible to assume that the center of the negative charges is more close to the neighboring positive charges Bi$^{5+}$ than the nucleus of the atom. The evaluated results are shown in the Table I, and are also shown in Fig.2 as a function of the bond length. We found that the stabilization energy $\Delta E$ is reduced linearly as a function of the bond length O-Bi(1) and becomes negative for about 10 percent movement. This indeed shows the stability of the observed CDW state.

Moreover, chemical bonding between Bi and O ions can further stabilize this CDW state. Bi$^{5+}$ ion can gain energy as the neighboring oxygen ions move toward it, lowering the energy of the oxygen states while raising the energy of the empty Bi s states, as compared to the Bi$^{3+}$ where those s-states are occupied. We consider Bi$^{5+}$ O$^{2–}$ cluster and the three-parameter model shown by Mattheiss and Hamann$^{[11]}$ for simplicity. Adopting more precise five-parameter model does not change the result seriously. The relevant orbitals are $|Bi – s >$ and $|O – A_{1g} > = (|p_1 > +|p_2 > +|p_3 > +|p_4 > +|p_5 > +|p_6 > )/\sqrt{6}$ orbitals, where $p_n > (n = 1, \ldots, 6)$ denotes the n-th oxygen p-orbital directing the Bi site. The secular equation is:

$$\left| \begin{array}{cc} \Delta - \epsilon & t \\ t & -\epsilon \end{array} \right| = 0$$

where $\Delta$ is the difference of the one-electron orbital energy $\Delta = \epsilon(Bi – s) - \epsilon(O – A_{1g})$, and $t$ is the effective transfer matrix $t = \sqrt{6}(sp\sigma)$. Using the well-known relation $(sp\sigma) \propto d^2 \sqrt{2}$ and the distortion $x = 0.26$, then the energy gain (loss) by the distortion is 0.42eV per electron for the bonding (antibonding) state. Since the Bi$^{5+}$ site has two empty states, thus the total energy gain is 0.84eV per Bi$^{5+}$. On the other hand, Bi$^{5+}$ ion cannot gain energy because there is no empty s-states. This effect apparently promotes forming the CDW state.

In the above discussion we only considered the insulating states. However, in the uniform BaBiO$_3$ the system may be metallic. In fact, band-calculations show that
uniform BaBiO₃ with no distortion and oxygen polarization should be metallic [11, 12]. The width of Bi6s band is about 4eV, and the Fermi level is just the middle of this band. Thus considering the small density of states at the bottom of this band, the average energy gain forming Bloch state is less than 1eV per electron. Each Bi³⁺ has one Bi6s electron, so that the total energy of the uniform state may go down less than 2eV. However, this value is not so large compared with the large energy gain of CDW state, and a further but little change of the negative charge, namely $x \sim 0.285$, can compensate this effect.

In order to further investigate the possibility of the negative $U$ originating from the long-range Coulomb interaction, we consider a state excited locally from the CDW ground state: a $(3+, 5+)$ Bi pair (e.g. Bi atoms at $(0,0)$ and $(0.5,0)$ in Fig.1) is changed into a $(4+, 4+)$ pair in the CDW background. The excitation energy for this process is

$$E_{\text{loc}} = \frac{1}{2}(V_{B1} - V_{B2}) - \frac{1}{2} \sum_i q_i \left( \frac{1}{r_i} - \frac{1}{|r_i - r_B|} \right)$$

Here $r_B = a_1 e_x$ denotes the position vector of Bi(2) at $e_x = (0.5, 0, 0)$, and $a_1$ is twice the average Bi-Bi distance ($a_1 = 8.700\AA$). $V_{B1}$ and $V_{B2}$ are the Madelung potential at the Bi(1) and Bi(2) site, respectively. The first term in eq.(12) is the change of the Madelung energy of the Bi pair, and the second term denotes that of the Madelung potential of the other ions. The third term shows the energy gain of the ionic (one-body potential) energy for $(3+, 5+) \rightarrow (4+, 4+)$, shown in eq.(9).

We performed the three-dimensional summation in real space for sites in the sphere of the radius $R$ using the procedure of Harrison [22]. This summation converged well for $R \sim 200a_0$ (see Ref.22). We do not suffer from the usual extreme oscillation of the potential in this case because we only consider the difference of the Madelung energy. Thus we do not need to add the $-Q/R$ term in contrast to the method in Ref.22. In the case of the Bi(1)-O bond-length $x = 0.282$, the local excitation energy is $E_{\text{loc}} = 6.92 + 10.56 - 10.7 = 6.78eV$. Hence the CDW state is stable against local valence fluctuation. Rice and Sneddon examined the low-energy effective Hamiltonian for the CDW state of BaBiO₃ and insisted that there are two types of excitations [23]. One is the single-particle excitation mentioned above, and the other is the two-particle excitation which is an exchange of local charges as $(3+, 5+) \rightarrow (5+, 3+)$. The excitation energy for $(3+, 5+) \rightarrow (5+, 3+)$ is extremely large because the second term of eq.(11) is twice as large as the process $(3+, 5+) \rightarrow (4+, 4+)$. From the definition of $U_n$ in eq.(8), the quantity $U_{4+}^{\text{local}} \equiv -E_{\text{loc}}$ resembles the intra-atomic energy. The value $U_{4+}^{\text{local}} = -6.78eV$ seems too large as the ‘negative’ $U$; the high dielectric constant and doped carriers, however, may reduce $E_{\text{loc}}$.

In summary, we have evaluated the Madelung potential for the valence skipping compound BaBiO₃ using the Ewald method. The total energy of the charge-ordered

| Bond length | Ba | Bi(1) | Bi(2) | O | $E_{\text{Madel}}/N_A$ | $\Delta E$ |
|-------------|----|-------|-------|---|-------------------|-------|
| 0.25        | (A) | -8.917 | -20.487 | 10.685 | -81.95       | 7.8   |
| 0.25        | (B) | -8.917 | -19.594 | 10.685 | -83.39       | 7.8   |
| 0.26        | (A) | -8.908 | -19.321 | 10.661 | -82.00       | 5.3   |
| 0.26        | (B) | -8.908 | -16.428 | 10.867 | -84.68       | 5.3   |
| 0.27        | (A) | -8.881 | -18.277 | 10.589 | -82.17       | 2.8   |
| 0.27        | (B) | -8.881 | -15.384 | 11.003 | -86.10       | 2.8   |
| 0.28        | (A) | -8.838 | -17.341 | 10.465 | -82.45       | 0.26  |
| 0.28        | (B) | -8.838 | -14.448 | 11.093 | -87.66       | 0.26  |
| 0.282       | (A) | -8.827 | -17.166 | 10.434 | -82.52       | -0.24 |
| 0.282       | (B) | -8.827 | -14.273 | 11.105 | -87.99       | -0.24 |

CDW state was calculated using the Madelung potential. We have evaluated the excitation energy for the local disorder $(3+, 5+) \rightarrow (4+, 4+)$ that is presumably realized if the center of the negative charges is moved from the center of the Bi-Bi bond by about 10 percent of the bond length. This indicates a possibility that the high critical temperature of BaBiO₃ is due to the valence-skipping induced negative $U$ as well as the electron-phonon interaction. The results also suggests that the elements with high electronic polarizability have strong possibility to induce negative $U$. Since the Te³⁻ ion has high polarizability [19], a negative $U$ induced superconductivity is likely present in Tl doped PbTe. The valence skip may provide a new idea for the material design of new superconductors.

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[1] C. M. Varma: Phys. Rev. Lett. 61 (1988) 2713.
[2] P. W. Anderson: Phys. Rev. Lett. 34 (1975) 953.
[3] W. A. Harrison: Phys. Rev. B74 (2006) 245128.
[4] C. Chailout, J. P. Remieka, A. Santoro, and M. Mareizo: Solid State Commun. 56 (1985) 829.
[5] L. F. Mattheiss, E. M. Gyorgy, and D. W. Johnson: Phys. Rev. B37 (1988) 3745.
[6] R. J. Cava et al.: Nature 332 (1988) 814.
[7] D. G. Hinks et al.: Nature 333 (1988) 836.
[8] H. Sato et al.: Nature 338 (1989) 214.
FIG. 1: The positions of bismuth and oxygen atoms in the plane of $z = 0$. Here we ignored the small tilting of BiO$_6$ octahedra.

[9] A. W. Sleight, J. J. Gilson, and P. E. Bierstedt: Solid State Commun. 17 (1975) 27.
[10] C. Chaillout, J. P. Remeika and A. Santoro: Solid State Commun. 65 (1988) 1363.
[11] L. F. Mattheiss and D. R. Hamann: Phys. Rev. B32 (1983) 4227.
[12] C. S. Ting, D. N. Talwar, and K. L. Ngai: Phys. Rev. Lett. 45 (1980) 1213.
[13] H.-B. Schuttler, M. Jarrell, and D. J. Scalapino: Phys. Rev. B39 (1989) 6501.
[14] A. G. Mal’shukov: Solid State Commun. 77 (1991) 57.
[15] A. Taraphder and P. Coleman: Phys. Rev. Lett. 66 (1991) 2814.
[16] Y. Ohnishi and K. Miyake; J. Phys. Soc. Jpn. 69 (2000) 3955.
[17] Y. Matsushita, H. Bluhm, T. H. Geballe, and I. R. Fisher: Phys. Rev. Lett. 94 (2005) 157002.
[18] M. Dzero and J. Schmalian: Phys. Rev. Lett. 94 (2005) 157003.
[19] C. Kittel: Introduction to Solid State Physics 8th ed. (New Jersey, John Wiley and Sons Inc., 2005). pp.644-648.
[20] J. Kondo: J. Phys. Soc. Jpn. 58 (1989) 2884.
[21] E. E. Cox and A. W. Sleight: Solid State Commun. 90 (1976) 969.
[22] W. A. Harrison: Phys. Rev. B73 (2006) 212103.
[23] T. M. Rice and L. Sneddon: Phys. Rev. Lett. 47 (1981) 689.
[24] K. Takegahara and T. Kasuya: J. Phys. Soc. Jpn.56 (1987) 1478.
[25] W. A. Harrison: Elementary Electronic Structure (World Scientific, Singapore, 1999), revised edition (2004).
FIG. 2: The Madelung potential at the Ba, Bi and O sites and the total energy as a function of the bond length. The solid lines and the dotted lines correspond to the case (A) and the case (B) (with the charge density wave), respectively. The bond length is normalized as 0.25 when there is no lattice relaxation.