

Madelung energy of the valence-skipping compound BaBiO₃

Izumi Hase and Takashi Yanagisawa

Condensed-Matter Physics Group, Nanoelectronics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 2, 1-1-1 Umezono, Tsukuba 305-8568, Japan

and CREST, Japan Science and Technology Agency (JST), Kawaguchi-shi, Saitama 332-0012, Japan

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Several elements show valence skip fluctuation, for instance, Tl forms the compounds in valence states +1 and +3 and Bi forms in +3 and +5 states. This kind of fluctuation gives rise to a negative effective attractive interaction and the Kondo effect. In the compounds of valence-skipping elements, the carrier doping will induce superconductivity with high critical temperature. For example, Ba_{1-x}K_xBiO₃ shows high T_c which is unlikely from the conventional electron-phonon mechanism. The reason for missing of some valence states in such valence skip compounds remains a mystery. We have performed the evaluation of the Madelung potential for BaBiO₃ and have shown that the 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. Tl and In form 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.¹⁻³ 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_xBiO₃ shows high T_c which is unlikely from the conventional electron-phonon interaction. A substitution of Ba with K for the compound BaBiO₃ provides superconductivity with T_c exceeding 30 K.⁴⁻⁸ Ba_{1-x}K_xBiO₃ is the perovskite three-dimensional superconductor with clear s -wave gap. The parent compound BaBiO₃ is an insulator though BaBiO₃ should be a metal according to the band theory.^{9,10} A band calculation within the local-density approximation leads to a (semi)metallic ground state of BaBiO₃,¹¹ even under the lattice distortion found in neutron-diffraction experiments. The average formal valence state of Bi is +4. The insulating state of BaBiO₃ would have spin 1/2 at the Bi site if Bi with +4 were allowed. BaBiO₃ is, however, the insulator with a charge density wave (CDW) gap of the order of 2 eV. The valence states +3 and +5 form the CDW state with average charge +4. The substitution of K for Ba induces carriers as doped holes leading to superconductivity, which is reminiscent of the phase diagram of cuprate high temperature superconductors. Since the high critical temperature found in Ba_{1-x}K_xBiO₃ may be unlikely from the conventional electron-phonon mechanism, one can expect that the negative- U attractive interaction would cooperate in promoting superconductivity.¹²⁻¹⁴

The valence skip is important in the study of a charge Kondo effect¹⁵ as well as valence-fluctuation induced superconductivity.¹⁶ A superconductor Pb_{1-x}Tl_xTe with $T_c = 1.4$ K (Ref. 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 of 1.5%, the material shows superconductivity with a remarkably high T_c as a low carrier metal. Tl impurities as negative- U centers could lead to superconductivity and at the same time Kondo effect as a charge analog.^{15,18}

The purpose of this paper is to investigate the mystery of missing valence states evaluating the intra-atomic energy for the Bi⁴⁺ 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 BaBiO₃. The curvature of the total energy as a function of the valence n , which is closely related to the intra-atomic energy U , may be presumably changed due to the Coulomb interaction. In the way stated, we calculate the Madelung energy of BaBiO₃. Letting 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 BaBiO₃. We assign the formal charges as

$$\text{Ba: } 2+, \quad \text{Bi: } 4+, \quad \text{O: } 2- \quad [\text{case (A)}], \quad (4)$$

TABLE I. Madelung potential in units of eV. The total electrostatic energy E_{Madel}/N_A and the stabilization energy of the CDW state ΔE defined in Eq. (10) are shown in units of eV. Note that E_{Madel}/N_A is for one BaBiO₃. The bond length between bismuth (1) and oxygen atoms is normalized as 0.25 when there is no lattice relaxation.

Bond length		Ba	Bi(1)	Bi(2)	O	E_{Madel}/N_A	ΔE
0.25	(A)	-8.917	-20.487	-20.487	10.685	-81.95	
0.25	(B)	-8.917	-17.594	-23.379	10.685	-83.39	7.8
0.26	(A)	-8.908	-19.321	-21.789	10.661	-82.00	
0.26	(B)	-8.908	-16.428	-24.681	10.867	-84.68	5.3
0.27	(A)	-8.881	-18.277	-23.244	10.589	-82.17	
0.27	(B)	-8.881	-15.384	-26.136	11.003	-86.10	2.8
0.28	(A)	-8.838	-17.341	-24.874	10.465	-82.45	
0.28	(B)	-8.838	-14.448	-27.766	11.093	-87.66	0.26
0.282	(A)	-8.827	-17.166	-25.223	10.434	-82.52	
0.282	(B)	-8.827	-14.273	-28.115	11.105	-87.99	-0.24

Ba: 2+, Bi(1): 3+, Bi(2): 5+, O: 2- [case (B)],
(5)

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 , and then the number of Bi and O atoms are N_A and $3N_A$, respectively. The total Madelung energy for case (A) is

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

$$= \frac{N_A}{2}(q_{Ba} V_{Ba} + q_{Bi} V_{Bi} + 3q_O V_O), \quad (6)$$

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

$$E_{Madel} = \frac{N_A}{2} \left(q_{Ba} V_{Ba} + \frac{1}{2} q_{Bi(1)} V_{Bi(1)} + \frac{1}{2} q_{Bi(2)} V_{Bi(2)} + 3q_O V_O \right), \quad (7)$$

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

$$U_n = E_{n+1} + E_{n-1} - 2E_n, \quad (8)$$

where E_i is the energy of the valence i state. The U for Bi⁴⁺ per two bismuth atoms has been estimated from the measured ionization energies of the elements as¹

$$U_{4+} = E_{ion}(\text{Bi}^{3+}) + E_{ion}(\text{Bi}^{5+}) - 2E_{ion}(\text{Bi}^{4+}) = 10.7 \text{ eV}. \quad (9)$$

Here, $E_{ion}(\text{Bi}^{n+})$ is the ionization energy of the element Biⁿ⁺. This estimated value is quite large, although it is smaller than that for Bi³⁺ ($U_{3+}=19.7$ eV) and Bi⁵⁺ ($U_{5+}=32.3$ eV). 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

$$\Delta E = E(\text{Ba}_2^{2+}\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6^{2-}) - E(\text{Ba}_2^{2+}\text{Bi}^{4+}\text{Bi}^{4+}\text{O}_6^{2-})$$

$$+ E_{ion}(\text{Bi}^{5+}) + E_{ion}(\text{Bi}^{3+}) - 2E_{ion}(\text{Bi}^{4+}), \quad (10)$$

where $E(\text{Ba}_2^{2+}\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6^{2-})$ and $E(\text{Ba}_2^{2+}\text{Bi}^{4+}\text{Bi}^{4+}\text{O}_6^{2-})$ are the total Madelung energies per two BaBiO₃'s, respectively. The charge-ordered state is stabilized if ΔE is negative. The Madelung potential V_a ($a=\text{Ba}$, Bi , and O) are shown in 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 BaBiO₃, 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 Table I. Apparently, case (B) with the charge density wave has the lower energy. From these values, we obtain $\Delta E=7.8$ eV, which is still positive. It is now important to notice that the ΔE 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.²¹ It has been reported by the neutron-diffraction experiment that the oxygen atoms are out of the center of two Bi ions by 4% of the Bi-O bond length due to lattice relaxation¹⁰ (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 Bi⁵⁺ than the nucleus of the atom. The evaluated results are shown in Table I and are also shown in Fig. 2 as a function of the bond length. We found that the stabilization energy ΔE is reduced linearly as a function of the bond length O-Bi(1) and becomes negative for about 10% movement. This indeed shows the stability of the observed CDW state.

Moreover, chemical bonding between Bi and O ions can

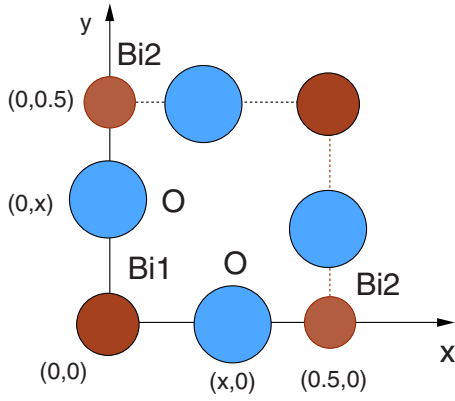


FIG. 1. (Color online) The positions of bismuth and oxygen atoms in the plane of $z=0$. Here, we ignored the small tilting of BiO_6 octahedra.

further stabilize this CDW state. The 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 the $\text{Bi}^{5+} \text{O}_6^{2-}$ cluster and the three-parameter model shown by Mattheiss and Hamann¹¹ for simplicity. Adopting a more precise five-parameter model does not change the result seriously. The relevant orbitals are $|\text{Bi}-s\rangle$ and $|\text{O}-A_{1g}\rangle = (|p_1\rangle + |p_2\rangle + |p_3\rangle + |p_4\rangle + |p_5\rangle + |p_6\rangle) / \sqrt{6}$ orbitals, where $|p_n\rangle$ ($n=1, \dots, 6$) denotes the n th oxygen p -orbital directing the Bi site. The secular equation is

$$\begin{vmatrix} \Delta - \epsilon & t \\ t & -\epsilon \end{vmatrix} = 0. \quad (11)$$

Here, Δ is the difference of the one-electron orbital energy, $\Delta = \epsilon(\text{Bi}-s) - \epsilon(\text{O}-A_{1g})$, and t is the effective transfer matrix $t = \sqrt{6}(sp\sigma)$. Using the well-known relation $(sp\sigma) \propto d^{-2}$ (Ref. 22) and the distortion $x=0.26$, then the energy gain (loss) by the distortion is 0.42 eV per electron for the bonding (anti-bonding) state. Since the Bi^{5+} site has two empty states, thus the total energy gain is 0.84 eV per Bi^{5+} . On the other hand, the Bi^{3+} ion cannot gain energy because there are 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 BaBiO_3 with no distortion and oxygen polarization should be metallic.^{11,23} The width of the Bi $6s$ band is about 4 eV, 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 the Bloch state is less than 1 eV per electron. Each Bi^{4+} has one Bi $6s$ electron, so that the total energy of the uniform state may go down less than 2 eV. However, this value is not so large compared with the large energy gain of the 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

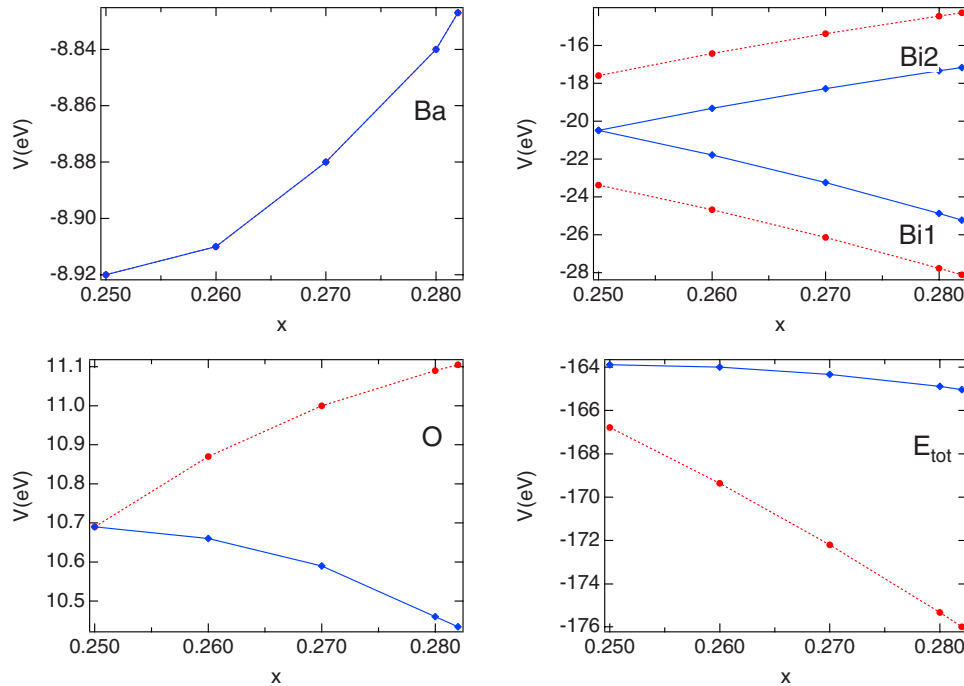


FIG. 2. (Color online) The Madelung potential at the Ba, Bi, and O sites and the total energy as a function of the bond length. The solid lines and the dotted lines correspond to cases (A) and (B) (with the charge density wave), respectively. The bond length is normalized as 0.25 when there is no lattice relaxation.

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

$$E_{loc} = \frac{1}{2}(V_{\text{Bi1}} - V_{\text{Bi2}}) - \frac{1}{2} \sum_i q_i \left(\frac{1}{r_i} - \frac{1}{|\mathbf{r}_i - \mathbf{r}_B|} \right) - U_{4+}. \quad (12)$$

Here, $\mathbf{r}_B = a_1 \mathbf{e}_x$ denotes the position vector of Bi(2) at $\mathbf{e}_x = (0.5, 0, 0)$, and a_1 is twice the average Bi-Bi distance ($a_1 = 8.700 \text{ \AA}$). V_{Bi1} and V_{Bi2} are the Madelung potentials at the Bi(1) and Bi(2) sites, 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.²⁴ This summation converged well for $R \sim 200a_0$ (see Ref. 21). 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. 21. In the case of the Bi(1)-O bond length $x=0.282$, the local excitation energy is $E_{loc} = 6.92 + 10.56 - 10.7 = 6.78 \text{ eV}$. Hence, the CDW state is stable against local valence fluctuation. Rice and Sneddon examined the low-energy effective Hamiltonian for the CDW state of BaBiO_3 and insisted that there are two types of excitations.²⁵ 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 $U_{4+}^{loc} \equiv -E_{loc}$ resembles the intra-atomic energy. The value $U_{4+}^{loc} = -6.78 \text{ eV}$ seems too large as the negative U ; the high dielectric constant and doped carriers, however, may reduce E_{loc} .

In summary, we have evaluated the Madelung potential for the valence-skipping compound BaBiO_3 using the Ewald method. The total energy of the charge-ordered CDW state was calculated using the Madelung potential. We have evaluated the excitation energy for the local disorder $(3+, 5+) \rightarrow (4+, 4+)$. It was shown that the polarization of electrons reduces the energy difference ΔE and that an attractive negative U is presumably realized if the center of the negative charges is moved from the center of the Bi-Bi bond by about 10% of the bond length. This indicates a possibility that the high critical temperature of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is due to the valence-skipping induced negative U as well as the electron-phonon interaction. The results also suggest that the elements with high electronic polarizability have strong possibility to induce negative U . Since the Te^{2-} ion has high polarizability,¹⁹ a negative U induced superconductivity is likely present in Tl doped PbTe. The valence skip may provide another idea for the material design of other superconductors.

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