Difference of Electronic Structures between $NaInO_2$ and $NaInS_2$

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The electronic structures of $NaInO_2$ and $NaInS_2$ are calculated by using the discrete variational X α method on model clusters. For $NaInO_2$, it is found that the In-O bonding is not perfectly ionic but partially covalent because of the hybridization between O 2s, 2p and In 5s, 5p orbitals in the electron-occupied band. However, the overlapping of Na 3s, 3p orbitals with O 2s, 2p orbitals is very weak. On the other hand, Na 3s, 3p orbitals of $NaInS_2$ relatively hybridize with S 3s, 3p orbitals, not only In 5s and 5p orbitals. These results show that the nature of the chemical properties of $NaInS_2$ is more covalent, compared with $NaInO_2$.

In general, a material group with the general formula ABX_2 (A: alkali-metal ion, B: trivalent ion, X: O, S or Se) crystallizes α-$NaFeO_2$ layer type structure. The space group of the unit cell is D^5_{3d} (R-3m) and it contains three ABX_2 formula.[1] Alternate layers of A and B atoms, separated by layer of X atoms, appear every 0.5c period in the c-axis direction. In the hexagonal system A, B and X occupy Wyckoff positions 3a, 3b and 6c respectively. The hexagonal unit cell can be also changed into the primitive rhombohedral unit cell, which contains one chemical formula.

These compounds are of interest, because they provide a chance to research for correlations between physical properties and chemical constitution systematically in a given crystal-structure. The most interesting aspect in ABX_2-type compounds is that compounds with identical A and B ions but different X ions exist which are insulators for X = 0 but semiconductors for X = S or Se.[2] Such the relationship between physical properties and chemical constitution is of theoretical interest from the standpoint of solid-state chemistry. To clarify the nature of ABX_2-type compounds, first of all, the important thing is to obtain correct information about the electronic structure of each material. However, no report is so far available about the electronic structure of α-$NaFeO_2$ layer type structure.

In the present study, we have performed a first-principles molecular orbital (MO) cluster calculation for $NaInO_2$ and $NaInS_2$ by discrete-variational (DV)-X α method and have elucidated the difference between the electronic structures of the two compounds.

A first-principles MO calculation has been carried out with a software[3] by the non-relativistic DV-X α method. Electronic structure of a model cluster has been self-consistently calculated using numerical atomic basis functions. The lattice parameters used are the same values as in bulk, a = 0.3232, c = 1.6390 nm for $NaInO_2$[4] and a = 0.3803, c = 1.9890 nm for $NaInS_2$.[5] The cluster model composed of 51 atoms $(Na_7In_6O_{38})^{51-}$ is employed in the MO calculation. The cluster is embedded in a Madelung potential generated by point charges outside the cluster. In the case of $(Na_7In_6O_{38})^{51-}$ cluster, total charge of the cluster^{51-} was obtained by counting the formal charges of Na^+, In^{3+} and O^{2-}. Similar calculation was also performed for $(Na_7In_6S_{38})^{51-}$ cluster.

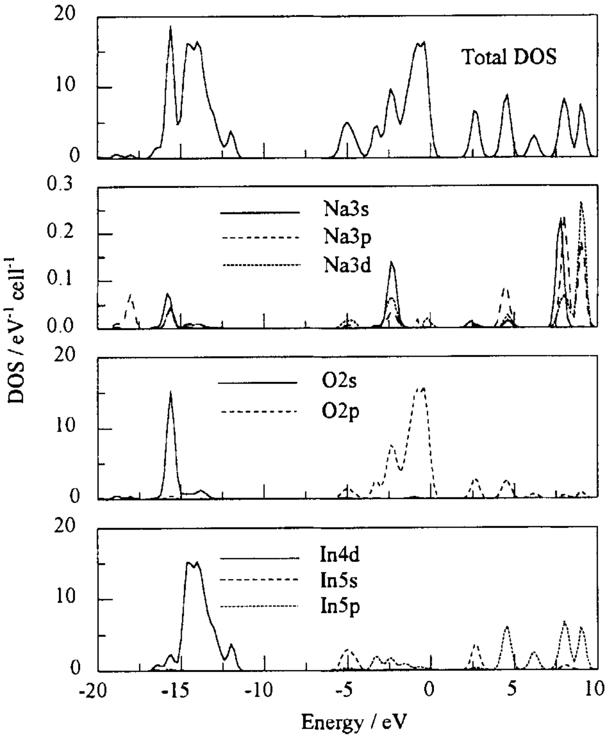


Figure 1. Total and partial density of states of $(Na_7In_6O_{38})^{51-}$ cluster.

Figure 1 shows total density of states (TDOS) and partial DOS (PDOS) for $(Na_7In_6O_{38})^{51-}$ cluster. Broadening the discrete energy eigenvalues makes all of DOS curves by Gaussian functions with 0.2 eV full width at half maximum. MO energies are aligned so as to make the highest occupied MO (HOMO) zero. The band gap between HOMO and the lowest unoccupied molecular orbital (LUMO) was 2.41 eV for $(Na_7In_6O_{38})^{51-}$. The valence band in the energy range from -6.0 to 0 eV is mainly constructed from O 2p orbitals, and they strongly hybridize with In 5s and 5p orbitals. The band at 0 eV is particularly constructed from O 2p orbitals (the contributions of In 5s and 5p orbitals are small). The conduction band from 2.0 to 5.0 eV is mainly constructed from In 5s and 5p orbitals. The presence of In 5s and 5p components in O 2p band region means that an In-O bonding is not perfectly ionic but partially covalent. This result is agreeing well with the calculation result that was obtained regarding In_2O_3.[6] On the other hand, the hybridizations of Na 3s, 3p and 3d orbitals with O 2s and 2p orbitals are very weak. This shows that for a Na-O bonding the ionic contribution is predominant because of a large electronegativity of oxygen and small ionization energy of a sodium atom.

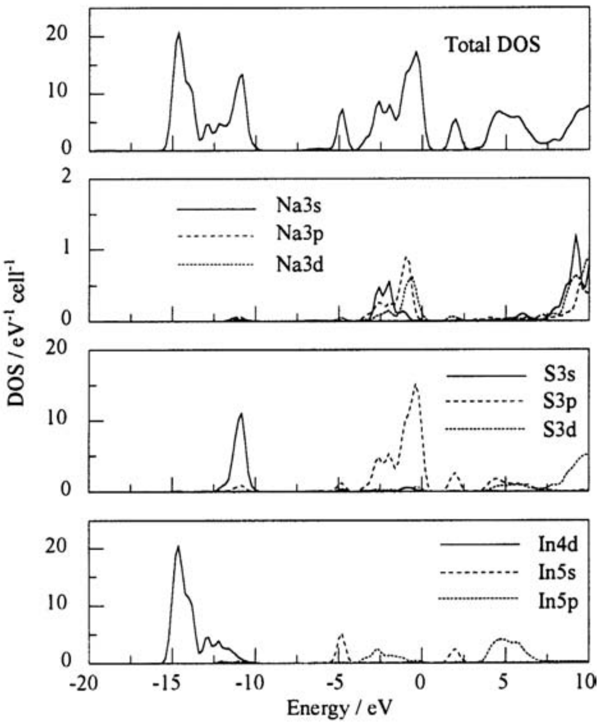
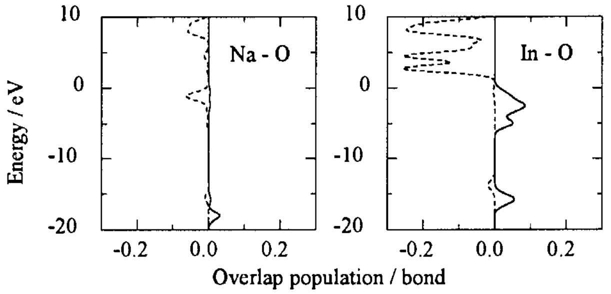


Figure 2. Total and partial density of states of $(Na_7In_6S_{38})^{51-}$ cluster.

(a) $[Na_7In_6O_{38}]^{51-}$



(b) $[Na_7In_6S_{38}]^{51-}$

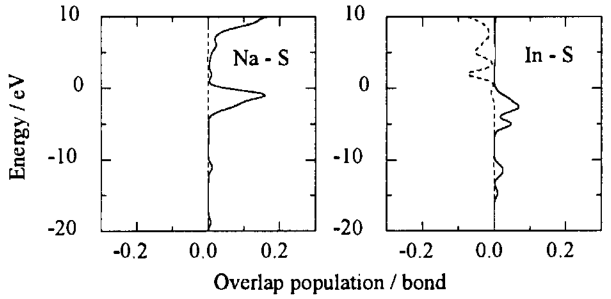


Figure 3. Overlap population diagrams for $(Na_7In_6O_{38})^{51-}$ and $(Na_7In_6S_{38})^{51-}$ clusters. Solid line shows the bonding contribution and dashed line the anti-bonding contribution.

Figure 2 shows the DOS curves that were obtained for $(Na_7In_6S_{38})^{51-}$ cluster. By changing the kind of anion, the energy gap between HOMO and LUMO decreased to 1.71 eV. This is agreeing with the general trend that an ionic crystal, which has the large difference between cation and anion in electronegativity, shows larger band gap than a covalent crystal.[7] Accordingly, this result is mainly explained by the fact that the electronegativity of sulfur is smaller than oxygen. Further, it should be noted that Na 3s, 3p, and 3d orbitals relatively hybridize with S 3s and 3p orbitals, not only In 5s and 5p orbitals. It is clear that the nature of the chemical bonding of Na-S is more covalent than that of Na-O in $NaInO_2$. Therefore, it is considered that the number of electrons on a Na atom increases and the covalent bond at a Na-S bonding strengthens.

Figure 3 (a) displays the overlap population diagrams for Na-O and In-O bonds obtained for the $(Na_7In_6O_{38})^{51-}$ cluster. The right part shows the bonding contribution and the left part the anti-bonding contribution. The nearest neighbors in the cluster (Na-O: 0.2161 nm, In-O: 0.2486 nm) were used in the overlap-population analysis. The In-O interaction shows a bonding contribution in the valence band region, although it shows an anti-bonding contribution in the conduction band region. The major part of the Na-O interaction belongs to an anti-bonding contribution. In addition, it was found that the O-O bond is less significant than the Na-O and In-O bonds. On the other hand, both In-S and Na-S interactions belong to a bonding contribution for the $(Na_7In_6S_{38})^{51-}$ cluster in the valence band region, as shown Fig. 3 (b). Furthermore, the Na-S interaction shows bonding contribution even in the conduction band region. This suggests that $NaInS_2$ is not only stable at the ground states but also at the excited states, where the conduction band is partially occupied by electrons.

Further studies by using spectroscopic measurements are in progress to obtain more detailed information for the difference of chemical properties between $NaInO_2$ and $NaInS_2$.

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