Comprehensive first-principles study of AgGaO₂ and CuGaO₂ polymorphs

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The electronic structures of delafossite-type α-AgGaO₂ and β-NaFeO₂-type β-AgGaO₂ were calculated based on density-functional theory using the local density approximation functional including the Hubbard correction. We compared the electronic structures of α- and β-AgGaO₂ with previously reported electronic structures of α- and β-CuGaO₂. We found that the Ag–Ag distances in α- and β-AgGaO₂ are almost the same as the Cu–Cu distances in α- and β-CuGaO₂, respectively, despite the ionic radius of Ag⁺ being larger than that of Cu⁺, because the frameworks of their crystal structures are determined by the linkages of GaO₆ octahedra in the α-phase and GaO₄ tetrahedra in the β-phase. It is indicated that transfer of electrons in Ag 4d states of AgGaO₂ can occur between Ag atoms more easily than in Cu 3d states of CuGaO₂ because high-electron-density regions surrounding Ag atoms are closer to each other than those of Cu atoms. This resulted in larger dispersion of the valence band of AgGaO₂ than CuGaO₂ for both α- and β-phases. We propose that the ratio of ionic radii of the monovalent and trivalent cations, \( \frac{r_{A^+}}{r_{B^{III}}} \), can provide an indication of the dispersion of the valence band of delafossite-type and β-NaFeO₂-type ternary oxide semiconductors.

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1. Introduction

Oxide semiconductors consisting of p-block cations, such as ZnO and SnO₂, generally possess wide band gaps in the UV region because of a strong contribution of highly ionic and deep O 2p states to the region around the valence band maximum (VBM).¹ By contrast, oxide semiconductors consisting of monovalent Ag⁺ or Cu⁺ have relatively narrow band gaps in the visible or near-IR regions because of significant contributions to the VBM region of Ag 4d or Cu 3d states, respectively, which are higher in energy than O 2p states. The shallow VBM of oxides containing Ag⁺ or Cu⁺ stabilizes the holes in the valence band and therefore often results in p-type conduction,¹ in contrast with common oxide semiconductors, which exhibit n-type conduction. In addition to the binary cuprite-type structure (Ag₂O and Cu₂O), well-known crystal structures of Ag⁺- or Cu⁺-containing oxide semiconductors are delafossite-type structures (α-phase; e.g., α-\( A^+B^{III}O₂ \), where \( A^+ = Ag \) or Cu and \( B^{III} = Al, Ga \) or In), and wurtzite-derived β-NaFeO₂-type structures (β-phase; e.g., β-\( A^+GaO₂ \) and β-\( AgAlO₂ \)) as shown in Fig. 1. Among them, AgGaO₂ and CuGaO₂ have been intensively studied for their unique properties; in particular, the band gaps of α- and β-AgGaO₂ are in the visible region (\( E_g = 2.4 \) and 2.2 eV, respectively).
respectively) and they are expected to be visible-light-responsive photocatalysts.β-CuGaO2 has a significantly narrow and direct band gap ($E_g = 1.47$ eV) and has been studied as a promising light absorber layer for solar cells.α-CuGaO2 is a p-type and transparent conductor, and has been studied as an absorber in dye-sensitized solar cells.

Because of the similar electronic configurations of Ag+ and Cu+, compounds containing these ions generally have the same crystal structure; examples of this are Ag2O and Cu2O, and α-AgGaO2 and α-CuGaO2. Although, first-principles studies have explored the differences in the electronic structures between α- and β-phases (e.g., between α- and β-CuGaO2,7,10 and between α- and β-AgGaO23), studies focusing on differences between Ag+ and Cu+ systems are limited. Therefore, first-principles study of AgGaO2 and CuGaO2 polymorphs will be helpful to relate the constituent atoms and crystal structures to their physical properties, and for establishing criteria to design new materials. The importance of such a study is increased by recent discoveries of novel oxide semiconductors with α- and β-phases (e.g., α-CuBO2 in 2007,8 β-Ag(Ga1-xAl)xO2 in 2011,4 β-CuGaO2 in 2014,5 β-Cu(Ga1-xAl)xO2 in 2017,10 β-NaFeO2-related-type Zn2LiGaO4 in 201111) and Cu2ZnGeO4 in 201712)).

In this study, we investigated the electronic structures of α- and β-AgGaO2, and compared them with our previous calculations of α- and β-CuGaO2.7 The local density approximation functional including the Hubbard correction (LDA+U) was used as the functional for α- and β-AgGaO2 to correct the strong electron correlation of Ag 4d electrons. First, we examined the validity of our calculations of α- and β-AgGaO2 by comparison with the experimentally obtained valence-band X-ray photoelectron spectra (XPS). We then compared the band structures of α-AgGaO2 and β-AgGaO2. Finally, we compared the band structures of AgGaO2 and CuGaO2 families and discussed how these band structures are determined by the constituent elements and crystal structures. Special focus was placed on the factors determining the dispersion of the valence band, which determines the hole mobility.

2. Methodology

2.1 Sample preparation for XPS analysis

β-AgGaO2 was synthesized by ion-exchange of Na+ in the precursor reaction with Ag+ from a molten salt of AgNO3 and KNO3, as previously reported.3,13 The obtained β-AgGaO2 was sintered by spark plasma sintering at 550°C for 15 min in vacuum under application of a uniaxial pressure of 10 MPa using a carbon die with an inner diameter of 20 mm. This resulted in a compact with a relative density of 47%, which was used for XPS analysis. α-AgGaO2 was obtained from β-AgGaO2 via phase transformation induced by heat treatment in water. Specifically, β-AgGaO2 powder was immersed in ultrapure water and kept at 60–70°C for 18 h in a reciprocal shaker, resulting in α-AgGaO2, as previously reported.3 The obtained α-AgGaO2 powder was pressed into 10-mm-diameter disks at 100 MPa and sintered at 500°C for 12 h under O2 flow of 100 mL min⁻¹ in a tubular furnace. This resulted in a compact with a relative density of 50%, which was used for XPS analysis.

2.2 XPS measurements

The electronic structure of the valence band of β-AgGaO2 was observed using hard X-ray photoelectron spectroscopy (HXPES). The HXPES spectra of β-AgGaO2 were recorded at the undulator beamline BL15XU of SPring-8 at room temperature. The X-ray photon energy was fixed at $h\nu = 5949.8$ eV. The mean free path of valence electrons with 6 keV kinetic energy was calculated as approximately 10 nm for β-AgGaO2. The total energy resolution, determined by measurement of the Fermi edge of pure Au, was approximately 0.2 eV. The binding energy of the system was calibrated using the C 1s line ($284.8$ eV)15) from the carbon contamination layer. In contrast with the β-phase, α-AgGaO2 was highly charged-up during the HXPES measurement because of the strong photon flux of the beamline. Therefore, we measured its valence band spectrum using laboratory-based XPS (i.e., a photoemission spectrometer with a hemispherical electron analyzer (Axis Ultra DLD, Kratos Analytical, UK) with monochromatic Ag Lα X-ray radiation ($h\nu = 2894.2$ eV)). The mean free path of valence electrons with 3-keV kinetic energy was calculated as approximately 5 nm for α-AgGaO2.14 The total resolution, determined from the Fermi edge of the Au films, was approximately 0.5 eV. The binding energy of the system was calibrated using the Au 4f7/2 core level at 84.0 eV of the Au film sputtered on a portion of the sample surface.

2.3 Computational method

All calculations based on density functional theory were performed using LDA+U16) as implemented in the CASTEP code.17) The norm-conserving pseudopotentials18) generated with OPIUM19) were used for the valence electrons of Ag 4d, 5s and 5p; Ga 3d, 4s and 4p; and O 2s and 2p. The Hubbard parameter, U, for Ag 4d electrons of Ag 4d, 5s and 5p; Ga 3d, 4s and 4p; and O 2s and 2p. The Hubbard parameter, U, for Ag 4d electrons was varied from 0 to 12 eV at 1-eV intervals to determine the most appropriate value based on the calculation reproducing the experimentally observed valence band from the HXPES or XPS spectra. Brillouin-zone sampling was performed with a 10 × 10 × 10 and $5 \times 4 \times 4$ k-point mesh for α- and β-AgGaO2, respectively. The plane-wave cut-off energy was set at 880 eV for all calculations. The geometry optimization for α- and β-AgGaO2 was imposed rhombohedral symmetry with the space group R3m and orthorhombic symmetry with the space group Pna21, respectively. The convergence conditions of the geometry optimization were as follows: the energy convergence tolerance was $5.0 \times 10^{-6}$ eV atom⁻¹, the maximum ionic displacement tolerance was $5.0 \times 10^{-4}$ Å, the maximum force tolerance was $1.0 \times 10^{-2}$ eV Å⁻¹, and the maximum stress tolerance was $2.0 \times 10^{-2}$ GPa.

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The calculated XPS spectra were generated from the cross-section-weighted density of states (DOS), which is the sum of the atomically projected partial DOS with each contribution weighted by a one-electron ionization cross-section for 3 keV and 6 keV, and spectral broadening of the instrumental resolution of 0.5 and 0.2 eV for \( \alpha \)-AgGaO\(_2\) and \( \beta \)-AgGaO\(_2\), respectively.

3. Results

3.1 Hubbard parameter, \( U \)

Values of the Hubbard parameters \( U \) for electrons in Ag 4d orbital of \( \alpha \)- and \( \beta \)-AgGaO\(_2\) were optimized based on the reproducibility of the electronic structure of the valence band with respect to the XPS spectra, as have previously done for LDA + U calculations of \( \alpha \)- and \( \beta \)-CuGaO\(_2\), where \( U \) was introduced for Cu 3d orbital.\(^{1,22)}\)

Figure 2 shows the valence-band XPS spectra of \( \alpha \)- and \( \beta \)-AgGaO\(_2\) calculated using LDA + U together with the experimentally observed spectra. In the calculated XPS spectrum of \( \alpha \)-AgGaO\(_2\) for LDA (without \( U \)), the main band, where the Ag 4d contribution is significant, appeared at approximately -4 eV, which is ~1.0 eV higher than the experimentally observed value (approximately -5 eV). When the parameter \( U \) was introduced into the LDA calculations and increased in value, the energy of the main band shifted to lower energies, similar to previous calculations for Cu(1)-containing oxides, such as \( \alpha \)-CuGaO\(_2\),\(^{7,23)} \( \beta \)-CuGaO\(_2\),\(^{23)} \) and Cu\(_2\)O.\(^{4,5)}\) The calculated energy of the main band of \( \alpha \)-AgGaO\(_2\) closely matched the experimentally observed energy for LDA + U with \( U = 2 \) and 3 eV.

When \( U \) was increased further to 4 eV, the energy of the main band became too low. In addition, for \( \beta \)-AgGaO\(_2\) [Fig. 2(b)], the energy and spectral shapes of the Ag 4d band and Ga 4s band closely matched the experimental spectrum for LDA + U with \( U = 2 \) and 3 eV. The crystal structure of \( \alpha \)- and \( \beta \)-AgGaO\(_2\) obtained by geometry optimization with \( U = 2 \)–3 eV reproduced well the experimentally observed structure\(^{23,26)}\) as summarized in Table S1 and S2 (see supporting information); in particular, the differences of the lattice parameters between calculated and experimentally-obtained were in between ~0.4 and +0.8% for \( \alpha \)-AgGaO\(_2\), and between -1.6 and +1.9% for \( \beta \)-AgGaO\(_2\). Therefore, we concluded that appropriate \( U \) values for both \( \alpha \)- and \( \beta \)-AgGaO\(_2\) are between 2 and 3 eV.

These \( U \) values were slightly smaller than those reported for \( \alpha \)-CuGaO\(_2\) (\( U = 3 \)–4 eV\(^{7)}\) and \( \beta \)-CuGaO\(_2\) (5–7 eV\(^{7)}\)). This can be explained as follows: the Ag 4d orbital has a larger radial extent than the Cu 3d orbital, because the ionic radius of Ag\(^+\) (1.0 and 0.67 Å for four- and two-fold coordination, respectively\(^{27)}\)) is much larger than that of Cu\(^+\) (0.60 and 0.46 Å). In other words, electrons of the Ag 4d orbital are less localized than those of the Cu 3d orbital.

Because the localization of electrons causes electron-correlation error, less-localized electrons (i.e., Ag 4d electrons), need a smaller correction parameter \( U \) than more-localized electrons (i.e., Ag 4d electrons). Similarly, a smaller \( U \) value for the Ag\(^+\)-containing oxide than the Cu\(^+\)-containing one was seen for Ag\(_2\)O (\( U = 2 \)–3 eV) and Cu\(_2\)O (\( U = 3 \)–4 eV) (Fig. S1, supporting information).

The calculated total energy of \( \beta \)-AgGaO\(_2\) was larger than that of \( \alpha \)-AgGaO\(_2\); in particular, the calculated total energies of the \( \beta \)-phase with \( U = 2 \) and 3 eV are, respectively, 59.2 and 55.7 kJ mol\(^{-1}\) larger than those of the \( \alpha \)-phase (Fig. S2, supporting information). This indicates that \( \alpha \)-AgGaO\(_2\) is thermodynamically more stable than \( \beta \)-AgGaO\(_2\). These values seem reasonable because they are of the same order of magnitude as the calculated total energy differences between \( \alpha \)- and \( \beta \)-CuGaO\(_2\) (-40 kJ mol\(^{-1}\)\(^{17)}\)) and the experimentally obtained heat of the transformation from \( \beta \)- to \( \alpha \)-CuGaO\(_2\) (32 kJ mol\(^{-1}\)\(^{29)}\))\(^{28)}\). Unfortunately, such a comparison in thermodynamic stability between \( \alpha \)- and \( \beta \)-AgGaO\(_2\) has not been reported. Nevertheless, the fact that \( \beta \)-AgGaO\(_2\) transforms to \( \alpha \)-AgGaO\(_2\) under moderate conditions (see section 2.1) and \( \alpha \)-AgGaO\(_2\) can be synthesized directly from Ag\(_2\)O and Ga\(_2\)O\(_3\) using hydrothermal or high-pressure techniques,\(^{29,30}\) provides strong implications that \( \alpha \)-AgGaO\(_2\) is more stable than \( \beta \)-AgGaO\(_2\), which is consistent with our calculations.

3.2 Band structures of \( \alpha \)- and \( \beta \)-AgGaO\(_2\)

Figure 3 shows the band structures of \( \alpha \)- and \( \beta \)-AgGaO\(_2\) calculated with LDA + U for \( U = 2 \) eV together with those of \( \alpha \)- and \( \beta \)-CuGaO\(_2\) taken from Ref. 7). \( \alpha \)-AgGaO\(_2\) had a VBM and CBM at the same points as \( \alpha \)-CuGaO\(_2\), which is consistent with our calculations.

\[ \text{Fig. 2. (a) Simulated XPS spectra of } \alpha \text{-AgGaO}_2 \text{ and (b) HXPS spectra of } \beta \text{-AgGaO}_2 \text{ based on LDA+U calculation with various values of } U. \text{ The bottom spectra were experimentally obtained by XPS (} \alpha \text{-AgGaO}_2 \text{) and HXPS (} \beta \text{-AgGaO}_2 \text{). The green, blue and red lines in the simulated spectra indicate the contribution of the Ag, Ga and O atoms, respectively.} \]
trast with \(\beta\)-CuGaO\(_2\), which is a direct semiconductor\(^7\) \(\beta\)-AgGaO\(_2\) was calculated to be an indirect semiconductor, which is consistent with the literature\(^4,33\). The CBM and VBM were, respectively, at the \(\Gamma\) point and the intermediate point between S and \(\Gamma\) points (see the enlarged version of \(E-k\) diagram in Fig. S3 in the supporting information). This VBM position is different from that reported in previous papers, in which it was located at the U point\(^4,33\). The dispersion of the valence band of \(\beta\)-AgGaO\(_2\) is so small that the position of the VBM varies depending on the calculation condition, as summarized in Table S3 (supporting information). Our result reproduced well the valence band XPS; therefore, our result is likely to be more reliable than those of previous calculations.

In Table 1, the calculated band gaps of \(\alpha\)- and \(\beta\)-AgGaO\(_2\) are summarized together with the experimentally determined values. The calculations underestimated the energy band gap for all cases, similar to the calculations for \(\alpha\)- and \(\beta\)-CuGaO\(_2\). This underestimation of the band gap is a common feature of LDA+U calculations even when appropriate values of \(U\) are used\(^2,3,34\).

In a previous comparison of \(\alpha\)-CuGaO\(_2\) and \(\beta\)-CuGaO\(_2\),\(^7\) there were two prominent differences in elec-
tronic structures, which were attributed to their crystal structures. Because of the similarity between Cu$^{+}$ and Ag$^{+}$, we make similar observations for $\alpha$- and $\beta$-AgGaO$_2$, as described below.

First, in the conduction band of the $\alpha$-phase, the contributions of Ag and Ga states are large at $\sim$3 and $\sim$6 eV, respectively, and therefore Ag and Ga states do not hybridize well in the whole range of the conduction band [Fig. 3(b)]. This difference is similar to that between $\alpha$- and $\beta$-CuGaO$_2$ and is attributed to the difference in the arrangement of the cations in the structures$^7$ Ag$_2$O (Cu$_2$O) and Ga$_2$O$_3$ layers alternatively stack and therefore Ag (Cu) and Ga atoms are spatially separated in the $\alpha$-phase [Fig. 1(a)], whereas Ag (Cu) and Ga atoms regularly replace the cation sites of wurtzite-type structures and therefore mix well in the $\beta$-phase [Fig. 1(b)]. Second, Ag 4d states in the valence band of the $\alpha$-phase exhibit larger dispersion than those of the $\beta$-phase [Figs. 3(a) and 3(b)]; this is consistent with the previously reported observation for $\alpha$- and $\beta$-CuGaO$_2$.$^7$ This is because the crystal field splitting of Ag 4d (Cu 3d) states of the $\alpha$-phase is much wider than that of the $\beta$-phase, reflecting the differences in local crystal structures around Ag (Cu) atoms.$^7$

3.3 Comparison between AgGaO$_2$ and CuGaO$_2$ polymorphs

The distributions of the DOS in the valence bands of the $\beta$-AgGaO$_2$ and $\beta$-CuGaO$_2$ are different [Figs. 3(b) and 3(d)]; the DOS of $\beta$-AgGaO$_2$ is spread over the range from 0 to approximately $-5$ eV, whereas the DOS of $\beta$-CuGaO$_2$ is significantly larger, in the range from 0 to approximately $2$ eV, and from approximately $-3.5$ to $-5$ eV. This difference becomes more distinct in the regions with no DOS in the valence bands [marked yellow in Figs. 3(b) and 3(d)], which correspond to the splitting of the bonding- and antibonding-states of Cu 3d/Ag 4d and O 2p states; the width of the splitting of $\beta$-CuGaO$_2$ ($\sim 1.5$ eV) is much greater than that of $\beta$-AgGaO$_2$ ($\sim 0.2$ eV). These results indicate that the valence band of $\beta$-AgGaO$_2$ has a larger dispersion than that of $\beta$-CuGaO$_2$. The difference in dispersions in the valence bands between $\beta$-AgGaO$_2$ and $\beta$-CuGaO$_2$ originates only from the difference in dispersions between Ag 4d and Cu 3d states, because there is almost no difference in the partial density of states (PDOS) of Ga and O in the valence bands between $\beta$-AgGaO$_2$ and $\beta$-CuGaO$_2$.

A similar difference can be seen between $\alpha$-AgGaO$_2$ and $\alpha$-CuGaO$_2$, although this was not as obvious as for the $\beta$-phases. The valence band of $\alpha$-AgGaO$_2$ has larger dispersion than that of $\alpha$-CuGaO$_2$; the PDOS of the Ag 4d states of $\alpha$-AgGaO$_2$ spread over the range from 0 to $-8$ eV, whereas that of Cu 3d states of $\alpha$-CuGaO$_2$ was restricted to the range of 0 to $-5$ eV with a large DOS from $-1.5$ to $-3.5$ eV. This difference arose solely from the difference in dispersion between Ag 4d and Cu 3d states, as was the case for the $\beta$-phases.

According to the results presented above, AgGaO$_2$ exhibits a larger dispersion of the valence band than CuGaO$_2$ for both $\alpha$- and $\beta$-phases. By contrast, simple oxides of Ag$_2$O and Cu$_2$O do not show a marked difference in the dispersions in their valence bands, as shown in Fig. 4. The PDOS of Ag 4d and Cu 3d states are distributed in a similar manner, although there is a slight difference in the peak position of the PDOS between Ag 4d and Cu 3d states, which reflects the different energies of their atomic orbitals. Therefore, we can assume that the difference in

![Fig. 4](image-url) Electronic band structure of (a) Cu$_2$O calculated with LDA+$U$ for $U = 4$ eV and (b) Ag$_2$O calculated with LDA+$U$ for $U = 2$ eV. (left) Band structures along the symmetry line with the horizontal axis standardized with respect to the length of each $k$ vector; (right) corresponding total and partial DOS.
valence-band dispersions of the Ag 4d states in AgGaO₂ and Cu 3d states in CuGaO₂ is due to these structures being a ternary system. In the following section, we discuss the reason for the difference in the dispersion of the Ag 4d and Cu 3d states.

4. Discussion

4.1 Factors determining the dispersion of the valence band

Table 2 shows the closest $A'$-$A'$ distances in the calculated structures of different oxides. For the simple oxides Cu₂O and Ag₂O, the size of the unit cell directly reflects the ionic radii of the constituent atoms; the Ag–Ag distance in Ag₂O (3.32 Å) is 8.9% longer than the Cu–Cu distance in Cu₂O (3.02 Å) because the ionic radius of Ag⁺ (0.67 Å for two-fold coordination) is much larger than that of Cu⁺ (0.46 Å for two-fold coordination). By contrast, for β-AgGaO₂ and β-CuGaO₂, the Ag–Ag distance in β-AgGaO₂ (3.32 Å) is only 2.8% longer than the Cu–Cu distance in β-CuGaO₂ (3.23 Å), even though the ionic radius of Ag⁺ (1.0 Å for four-fold coordination) is significantly larger than that of Cu⁺ (0.6 Å for four-fold coordination). This can be explained based on how the crystal structures of β-NaFeO₂-type oxides are built up as follows. The framework of the β-NaFeO₂-type structure is mostly formed by linkages of GaO₂⁻, which connect GaO₂ tetrahedra, because GaO₂ tetrahedra are difficult to distort from the ideal tetrahedron and keep almost the same size and shape regardless of whether the monovalent cation is Ag⁺ or Cu⁺. Therefore, the Ag–Ag and Cu–Cu distances are almost the same in β-AgGaO₂ and β-CuGaO₂. A similar observation can be made for the α-phases. The size of the a–b plane of the α-phases, where adjacent $A'$–$A'$ connections exist, is determined only by the size of the trivalent cations; therefore, the Ag–Ag distance in α-AgGaO₂ (3.01 Å) is exactly the same as the Cu–Cu distance in α-CuGaO₂ (3.01 Å). As a result, the $A'$–$A'$ distance in ternary oxides is almost constant, regardless of the radius of $A'$, as long as the trivalent cations are the same.

To compare the Cu 3d and Ag 4d states in these materials, two-dimensional electron-density contour plots of the valence bands were obtained and are shown in Fig. 5. The high-electron-density regions surrounding Ag and Cu atoms are attributed to their Ag 4d and Cu 3d states based on the PDOS (Figs. 3 and 4). Because Ag⁺ has a larger ionic radius than Cu⁺, the high-electron-density regions surrounding Ag atoms in all materials are more extended than those surrounding Cu atoms. The width of the low-electron-density region between adjacent Ag atoms in Ag₂O (1.47 Å) is very close to that between Cu atoms in Cu₂O (1.38 Å) with a difference of only 0.09 Å [Figs. 5(a) and 5(b)]. By contrast, the width of the low-electron-density region between adjacent Ag atoms in β-AgGaO₂ (0.98 Å) is much smaller than that between Cu atoms in β-CuGaO₂ (1.28 Å) with a difference of 0.3 Å. In addition, the width of the low-electron-density region in α-AgGaO₂ (1.07 Å) is much smaller than that in α-CuGaO₂ (1.30 Å). A small width of the low-electron-density region between Ag atoms means that electron transfer between adjacent Ag atoms occurs easily (i.e., the electrons in Ag 4d states are more delocalized). Therefore, this observation is consistent with the result that AgGaO₂ exhibited larger dispersion of the valence band than CuGaO₂ (Fig. 3).

On the basis of the results above, the ratio of ionic radii of the monovalent and trivalent cations, $r_{A'/rgm}$, can indicate the dispersion of the valence band; that is, a larger dispersion is expected for a larger $r_{A'/rgm}$, and vice versa. More specifically, when the trivalent cation is small (i.e., $r_{A'/rgm}$ is large), the $A'$–$A'$ distance becomes shorter; therefore, the width of the low-electron-density regions between adjacent monovalent cations become narrow, resulting in a larger dispersion of the valence band. When the monovalent cation is large (i.e., $r_{A'/rgm}$ is large), the width of the low-electron-density regions is narrow and results in a large dispersion of the valence band, because the $A'$–$A'$ distance is almost exclusively determined by the size of the trivalent cation.

Figure 6 shows the relationship between $r_{A'/rgm}$ and the smallest calculated hole effective mass of delafossite-type and β-NaFeO₂-type oxide semiconductors. For delafossite type α-ABO₂, an oxide with a larger $r_{A'/rgm}$ has a smaller hole effective mass, which is consistent with the discussion above. For β-NaFeO₂-type oxide semiconductors, it is not possible to compare β-CuGaO₂ and β-AgBO₂ directly because they are direct and indirect semiconductors, respectively, having VBM at different $k$-points (the effective masses only depend on the curvature of a very narrow region around the VBM). Nevertheless, comparing β-AgAlO₂ and β-AgGaO₂, which are both indirect semiconductors, the former is smaller than the latter; this is also consistent with the discussion above.

On the basis of the discussion above, ternary oxide semiconductors with large dispersions of the valence band (i.e., the high hole mobility) can be realized for α- and β-phases in the following ways. Delafossite-type oxide semiconductors can contain many trivalent cations, such as B, Al, Ga, In, Cr and Rh; therefore, it is possible to control the dispersion of the valence band by alloying these trivalent cations and monovalent cations. Recently, a new delafossite-type oxide, α-CuBo₂, was found, which has a small effective mass. β-NaFeO₂-type oxide semiconductors can only contain Ga⁺, Al³⁺ and Fe³⁺ as trivalent ions; therefore, for example, substitution of Ga³⁺ in β-

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**Table 2.** Closest distance of monovalent atoms ($A'$–$A'$, $A'$ = Cu, Ag) in crystal structures of several oxides obtained by geometry optimization with LDA+U. Shannon’s ionic radii of monovalent atoms for corresponding coordination are taken from Ref. 27.

| Material       | Calculated $A'$–$A'$ (Å) | Ionic radius of $A'$ (Å) |
|----------------|---------------------------|--------------------------|
| Ag₂O          | 3.29                      | 0.67                     |
| Cu₂O          | 3.02                      | 0.46                     |
| α-AgGaO₂      | 3.01                      | 0.67                     |
| α-CuGaO₂      | 3.01                      | 0.46                     |
| β-AgGaO₂      | Ave. 3.32                 | 1.00                     |
| β-CuGaO₂      | Ave. 3.23                 | 0.60                     |
CuGaO$_2$ with smaller Al$^{3+}$ will lead to a larger $r_{Al}/r_{Ga}$ and larger dispersion of the valence band. Another way to realize a large $r_{Al}/r_{Ga}$ is by substituting Cu$^+$ with the larger-radius Ag$^{+}$, considering that Ag 4d and Cu 3d states hybridize well (e.g., in AgCuO$_3$ or Cu$_2$-Ag$_x$O$_4$). We note here that Nagatani et al. also used the same index, $r_{Al}/r_{Ga}$, for $\beta$-NaFeO$_2$-type oxide semiconductors to relate the distortion of the crystal structure to the nature of band gap, i.e., direct or indirect. The hypothesis of that study was that oxides with $r_{Al}/r_{Ga} \sim 1$ (e.g., $\beta$-CuGaO$_2$ and $\beta$-LiGaO$_2$ with values of 1.26 and 1.28, respectively) are direct semiconductors, and those with $r_{Al}/r_{Ga} \gg 1$ (e.g., $\beta$-AgGaO$_2$ and $\beta$-AgAlO$_2$ with values of 2.13 and 2.56, respectively) are indirect semiconductors. Therefore, $\beta$-NaFeO$_2$-type oxides that have a direct band gap and dispersion larger than that of $\beta$-CuGaO$_2$ can be realized by alloying $\beta$-CuGaO$_2$ with another $\beta$-NaFeO$_2$-type oxide by keeping $r_{Al}/r_{Ga}$ close to 1. Examples of this are $\beta$-Cu$_1$-Ag$_x$Ga$_O_2$ and $\beta$-Cu$_1$-Al$_x$O$_2$, which was synthesized recently.

![Fig. 5. Two-dimensional electron-density counter plots of (a) Cu$_2$O within the energy range ($E-E_{VBM}$) of $-7.50-0$ eV of the (111) plane, (b) Ag$_2$O within the energy range of $-7.89-0$ eV of the (111) plane, (c) $\beta$-CuGaO$_2$ within the energy range $-2.16-0$ eV located at $z = 0.5057$, (d) $\beta$-AgGaO$_2$ within the energy range of $-2.55-0$ eV located at $z = 0.5120$, (e) $\alpha$-CuGaO$_2$ within the energy range $-6.82-0$ eV located at $z = 0$ and (f) $\alpha$-AgGaO$_2$ within the energy range $-7.01-0$ eV located at $z = 0$. The values indicated in the figures are the widths of the low-electron-density regions between adjacent Cu or Ag atoms.](image-url)
The black and green lines show the arrangement of the cations in the crystal structures.

The conduction bands are strongly and poorly mixed in the (Cu) atoms. In addition, Ag (Cu) and Ga states in the crystal structures is determined by the linkages of GaO$_6$ octahedra in the α-phase and GaO$_4$ tetrahedra in the β-phase, the Ag–Ga distance in CuGaO$_2$ and in the Cu–Ga distance in CuGaO$_2$ are almost the same, although the ionic radius of Ag$^+$ is much larger than that of Cu$^+$. Therefore, transfer of electrons in Ag 4d states between Ag atoms can occur more easily than in Cu 3d states. This is the origin of the larger valence-band dispersion of AgGaO$_2$ than CuGaO$_2$. To generalize this trend, the ratio of ionic radii of the monovalent and trivalent cations, $r_{A^+}/r_{B^{3+}}$, can provide an indication of the dispersion of the valence band of delafossite-type and β-NaFeO$_2$-type ternary oxide semiconductors; that is, a larger $r_{A^+}/r_{B^{3+}}$ indicates a larger valence-band dispersion and vice versa. We expect that this study will improve our understanding of the physical properties of ternary oxide semiconductors and contribute to the design of the novel oxides related to these crystal structures.

5. Conclusions

We calculated the electronic structures of delafossite-type α-AgGaO$_2$ and β-NaFeO$_2$-type β-AgGaO$_2$ and compared these with those previously reported for α- and β-CuGaO$_2$. Because of the similar electronic configuration of Ag and Cu atoms, the differences between the electronic band structures of α- and β-AgGaO$_2$ were similar to those between α- and β-CuGaO$_2$. Specifically, α-phases have larger valence-band dispersion than β-phases, reflecting differences in the local structure surrounding Ag (Cu) atoms. In addition, Ag (Cu) and Ga states in the conduction bands are strongly and poorly mixed in the α- and β-phases, respectively, reflecting differences in the arrangement of the cations in the crystal structures. When α- and β-AgGaO$_2$ were compared with α- and β-CuGaO$_2$, the valence band of AgGaO$_2$ exhibited larger dispersion than that of CuGaO$_2$ for both α- and β-phases. This is explained as follows. Because the framework of the crystal structures is determined by the linkages of GaO$_6$ octahedra in the α-phase and GaO$_4$ tetrahedra in the β-phase, the Ag–Ga distance in AgGaO$_2$ and the Cu–Ga distance in CuGaO$_2$ are almost the same, although the ionic radius of Ag$^+$ is much larger than that of Cu$^+$. Therefore, transfer of electrons in Ag 4d states between Ag atoms can occur more easily than in Cu 3d states. This is the origin of the larger valence-band dispersion of AgGaO$_2$ than CuGaO$_2$. To generalize this trend, the ratio of ionic radii of the monovalent and trivalent cations, $r_{A^+}/r_{B^{3+}}$, can provide an indication of the dispersion of the valence band of delafossite-type and β-NaFeO$_2$-type ternary oxide semiconductors; that is, a larger $r_{A^+}/r_{B^{3+}}$ indicates a larger valence-band dispersion and vice versa. We expect that this study will improve our understanding of the physical properties of ternary oxide semiconductors and contribute to the design of the novel oxides related to these crystal structures.

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