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Insight into the origin of superionic conductivity from electronic structure theory

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Abstract. We study the electronic properties of a series of tellurides with the antifluorite structure, Ag_2Te , Cu_2Te and M_2Te ($\text{M} = \text{Li}, \text{Na}, \text{K}$), to reveal the outstanding diffusivity of silver ions. We carry out first-principles density-functional calculations for these systems using the linearized augmented-plane-wave (LAPW) method, where the exchange–correlation effects of electrons are treated in the local density approximation. The calculations illuminate the difference in the outermost electron configurations between the noble-metal (d-shell) and the alkali (sp-shell) ions. The noble-metal ions embedded in the Te sublattice with the p valence band are far more deformable in the crystalline field than the alkali ions are. We then elucidate that Ag_2Te and Cu_2Te have remarkably different degrees of p–d hybridization. The d states of Ag atoms are much more weakly coupled with the p states of Te atoms and hence keep their localized nature. The activation energies for the ionic diffusion are evaluated to show that the Ag ion has a smaller barrier as compared with the alkali and copper ions in the Te framework. It is thus inferred that the superionic conductivity of Ag ions primarily stems from combination of the deformability of the d shell and the weakness of the p–d hybridization. To confirm this conclusion, we also apply the LAPW calculation to AgI in the γ -phase.

1. Introduction

The noble-metal atoms form halides and chalcogenides with various kinds of novel physical property including superionic conductivity [1–5]. Ionic compounds such as AgI, CuI, Ag_2Te and Cu_2Te show large ionic conductivities comparable to those of electrolyte solutions well below their melting temperatures; anions form a stable, ordered lattice and cations migrate through the sublattice. The superionic conductors have thus attracted not only academic but also the technological interest of a number of researchers.

Molecular dynamics (MD) simulations [2, 3, 5] have been successfully applied to the silver superionic conductors to elucidate the diffusion processes of Ag ions jumping between energetically favoured residence sites in the framework of the stable anion lattices. The MD studies, however, critically depend on empirical interatomic potentials with free parameters adjusted to reproduce the experimental results. The steric size of Ag ions used in the MD simulations is remarkably small as compared with the representative ionic radius due to Pauling [6], who fruitfully replaced ions by charged hard spheres in order to discuss the structural stability of ionic compounds. The MD radius for Ag ions is only half of that of

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Pauling; Ag ions are much larger than Li ions and even larger than Na ions according to him. The MD simulations are thus no help in finding an answer to such a fundamental question as why the relatively large ion shows the anomalously large conductivity; its mechanism is built into the MD potentials at the outset. This issue clearly originates from characteristics of the electronic properties of the superionic conductors.

The noble-metal ions are distinguished from the alkali ions by their possession of a closed d shell. Since the spatial extent of the d levels is large and their energies are close to those of the p valence levels of halogen and chalcogen atoms, it has been naturally conjectured [7–9] that the p and d levels are strongly hybridized and thus significantly alter the physical properties of the compounds. Fedorin [10] thus proposed that the superionic conductivity arose from the strong hybridization between the d states of the noble-metal atoms and the p states of the host anions; more detailed modelling was later given [11] for the superionic transition in the silver halides. Alternatively, quadrupolar deformability of the d shell of Ag ions was introduced [12, 13] to interpret the anomalous lattice dynamics of silver halides (significant reduction of the transverse optic frequencies and the elastic shear constant) and then was shown [14, 15] to lead to a decrease of the activation energy for ionic diffusion. These two ideas more or less contradict each other, however. The claim for importance of the p–d hybridization in the superionic transition emphasizes bandlike behaviour of the d electrons, while the aspect of the deformability of the d shell implicitly assumes that those electrons keep atomic characters in the solid state. We should note here that there is marked difference even between the noble-metal ions as regards the ionic conductivity: the Ag ion is more mobile than the Cu ion in compounds although the former ion has a larger steric size than the latter [16–18].

In the present paper we shed light on the origin of the superionic conductivity of Ag ions using electronic structure theory based on first-principles density-functional calculations [19–22]. The systems studied here are Ag_2Te , Cu_2Te and M_2Te ($\text{M} = \text{Li}, \text{Na}, \text{K}$) with the antifluorite structure as well as AgI in the γ -phase with the zinc-blende structure. Ag_2Te in the α -phase ($400 \text{ K} \lesssim T \lesssim 1000 \text{ K}$), a typical superionic conductor, takes basically the antifluorite form as an averaged crystalline structure. γ -AgI is a metastable low-temperature state prior the superionic transition. Compilation of the band calculations for these systems enables us to discuss the fundamental issue raised here concerning the ionic transport in superionic conductors. Partial accounts of the present study have already been given elsewhere [23, 24].

2. The target systems and computational method

In α - Ag_2Te the Ag ions migrate through an FCC sublattice formed by the Te atoms. We replaced such a disordered structure in α - Ag_2Te by a crystal with the antifluorite structure. The replacement is justified by diffraction measurements [25, 26] indicating that the Ag ions distribute around the tetrahedral sites with appreciably greater probability than around the octahedral sites in the α -phase; an FCC lattice structure is composed of two kinds of polyhedron, namely tetrahedra and octahedra. We also studied isostructural tellurides with the Ag atoms substituted for with Cu, Li, Na or K atoms for comparative analyses. As regards AgI, another representative compound studied here, there is no sound basic structure for the superionic conducting phase in which iodine atoms form a BCC sublattice. We therefore turned our attention to the γ -phase with well-defined crystalline order. The two structures are illustrated in figure 1.

We employed the linearized augmented-plane-wave (LAPW) method [27–29] to calculate the electronic band structure on the basis of the Kohn–Sham (KS) scheme in

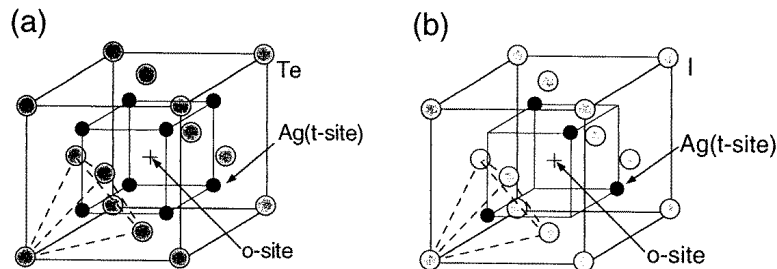


Figure 1. Antifluorite (a) and zinc-blende (b) structures for α - Ag_2Te and γ - AgI . The designations t and o refer to the 8c sites (tetrahedral sites) and the 4b sites (octahedral sites) in the iodine sublattice with the FCC structure, respectively.

the density-functional theory. The exchange–correlation energy functional was treated in the local density approximation. The muffin-tin (MT) approximation was applied to both the potential and the electronic density to speed up the self-consistent solution of the KS equation. In addition to the atomic MT spheres, however, we placed MT spheres at empty sites with relatively high symmetry to take account of anisotropic effects due to the crystalline structure. In contrast to the conventional APW calculations, the present calculation treated the radii of those MT spheres as variable parameters in the framework of the energy variational principle in the density-functional theory. Such variational treatment of the MT sphere radii is indispensable to correctly reproducing various electronic properties of the ionic compounds including the semiconducting nature of α - Ag_2Te . The lattice constants were also determined through minimization of the total energy. For details of the computational method, we refer the reader to the references [23, 30].

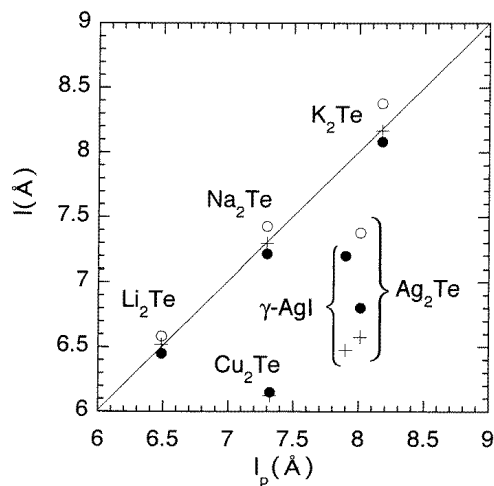


Figure 2. Lattice constants l obtained either theoretically or experimentally versus the corresponding values l_p predicted with Pauling's ionic radii. The filled and open circles refer to the results calculated with and without the empty MT spheres, respectively; the crosses refer to the experimental results.

3. Deformability of the d shell

The predictive power of the present calculations is exemplified in figure 2, where the theoretical lattice constants are compared with the experimental values. The lattice constants are reproduced within errors of 3% except for γ -AgI. Figure 2 also compares those results with the corresponding lattice constants based on Pauling's ionic radii.

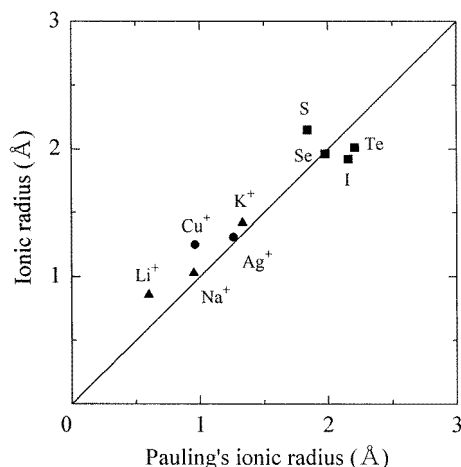


Figure 3. Comparison between the ionic radii due to Pauling (plotted with reference to the horizontal axis) and those determined from the electronic density distributions of individual ions (plotted with reference to the vertical axis); for the criterion for the latter quantity, refer to the text. The radii of individual anions are replaced by those of the corresponding neutral atoms.

We immediately find that the noble-metal compounds shrink substantially by comparison to Pauling's values, while the lattice constants of the alkali tellurides are explained fairly well by his idea. Such peculiar shrinking indicates the deformability of the noble-metal ions with the d shells. The experimental (theoretical) radii of the Cu and Ag ions extracted from the lattice constants of their tellurides are 0.44 (0.45) Å and 0.64 (0.73) Å, respectively, where the radius of Te^{2-} is taken to be that of Pauling, 2.21 Å. The radii of the noble-metal ions are markedly smaller than Pauling's assignments, 0.96 Å and 1.26 Å, for Cu^+ and Ag^+ , as has been manifested by the MD simulations. However Pauling's radii represent quite well the actual size of the ions in the isolated state. To confirm that, we defined the radii of isolated ions through density-functional calculation of the electronic density distributions. We arbitrarily assumed that 98.6% of the total population of electrons is contained inside the defined ionic sphere. Figure 3 compares the radii so determined for relevant ions with the corresponding ionic radii due to Pauling. We thus see good correlation between the two quantities; at least the relative ordering in the size of the isolated ions is reflected by Pauling's radii.

Alternatively, the deformability of Ag^+ can be appreciated by considering the following fact. The accuracy of the LAPW calculation for Ag_2Te was improved by the MT spheres being placed at the empty octahedral sites in a much more significant way than for the alkali counterparts. This indicates that the shape of Ag^+ is modified by the crystalline field while the alkali ions keep their round shape in forming the compounds. Since the zincblende structure is highly anisotropic, however, introduction of the MT spheres at the empty tetrahedral and octahedral sites is not so effective in improving the prediction for γ -AgI.

Table 1. Reduced multipole polarizabilities for closed-shell cations. The quadrupole and octupole polarizabilities, α_q and α_o , for each cation are normalized in terms of the corresponding ionic radius σ_P due to Pauling. The results are based on the data given in [31]; the numbers in the parentheses are based on those in [32].

	Li ⁺	Na ⁺	K ⁺	Cu ⁺	Ag ⁺
α_q/σ_P^5	0.059 (0.075)	0.052 (0.094)	0.14 (0.20)	0.75 —	0.42 (0.82)
α_o/σ_P^7	0.064 (0.093)	0.040 (0.10)	0.11 (0.19)	2.1 —	0.35 (0.89)

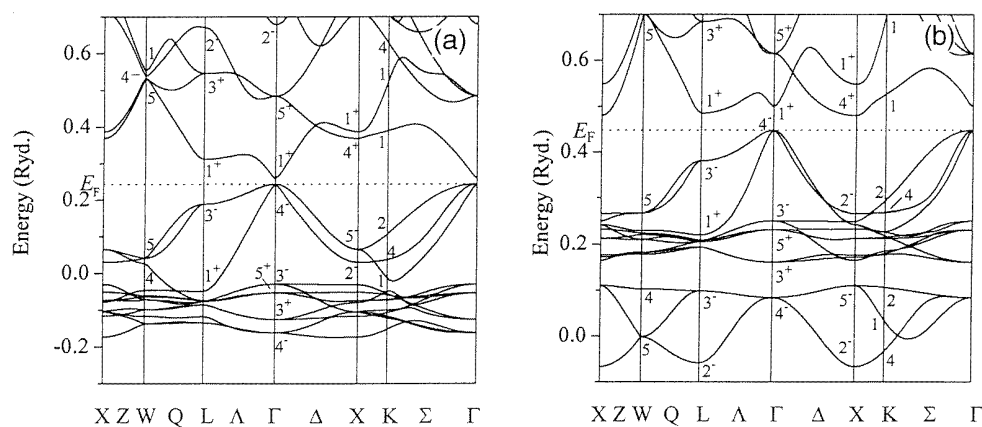


Figure 4. Band structures of Ag₂Te (a) and Cu₂Te (b), calculated at the equilibrium lattice constants. Bethe's notation is used for the irreducible representations. E_F denotes the Fermi energy.

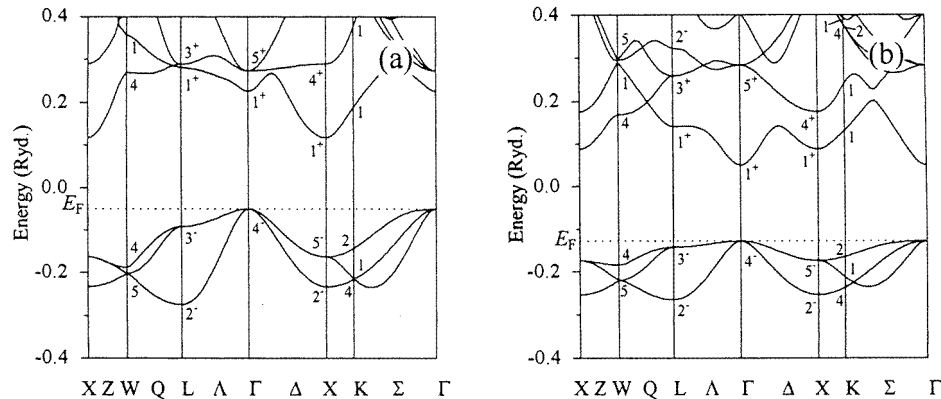


Figure 5. Band structures of Li₂Te (a) and Na₂Te (b), calculated at the equilibrium lattice constants.

In passing it is worth recalling the density-functional calculations for the multipole polarizabilities of closed-shell ions made by Mahan [31, 32]. We have normalized his results, given in ångströms, in terms of Pauling's radii to remove the nominal dependence on the dimension of ions. The quadrupole and octupole polarizabilities should scale as the fifth and seventh powers of the ionic radii, respectively. The results for relevant cations are

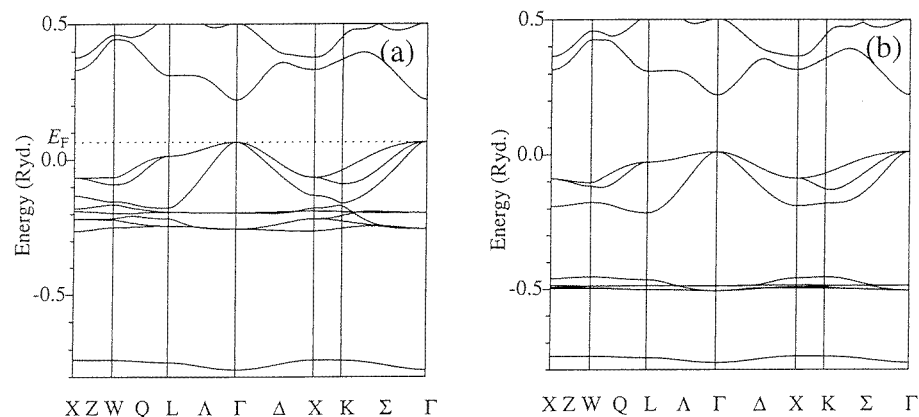


Figure 6. Panel (a) shows the band structure of γ -AgI, calculated at the experimental lattice constant; panel (b) shows the recalculated version with a selective downward shift of the d band by 0.3 Ryd.

listed in table 1. The reduced polarizabilities thus reveal the deformability of the noble-metal ions.

4. Coupling between the p and d valence states

Figure 4 shows the band structures of Ag_2Te and Cu_2Te calculated at the equilibrium lattice constants. The theoretical calculation correctly reproduces the semiconducting nature of α - Ag_2Te with a band gap of 0.2 eV, which is in good agreement with the experimental value of around 0.1 eV [33]. We also confirmed that the effective masses of electrons and holes near the band gap and the density of states agree well with experimental results for α - Ag_2Te [23]. Although the d levels of the noble-metal atoms are located close to the p levels of the Te atom, the two bands arising from those states are graphically well separated for both compounds. However, there are remarkable differences as regards the electronic structure. The d band in Ag_2Te is much narrower than that in Cu_2Te , and the relative positions of the d and p bands are interchanged between the two compounds. As seen in figure 5, the band-structure calculations for the alkali tellurides show that the essential features of the p band observed in Ag_2Te remain unchanged irrespective of the absence of the d band, indicating weak hybridization of the Ag d states and Te p states. We also applied the present computational scheme to γ -AgI, but with the experimental lattice constant. Panel (a) in figure 6 demonstrates that the relationship between the p and d bands in γ -AgI shares the same characteristics as in the case of Ag_2Te . The band structure agrees well with the recent calculation [34] based on a different computational method.

The density of states calculated from the band structure of γ -AgI is shown in figure 7 along with the photoelectron energy distribution curve. We see that the theoretical calculation reproduces all of the characteristic features observed in the experiments [7]. Once again the reliability of the present calculations is demonstrated. The theoretical densities of states are also decomposed into the partial contributions, and we find appreciable overlap between the I p and Ag d components. This result, which may contradict our earlier findings, corroborates previous studies [7–9] based on the photoelectron spectrum and model band calculations for a wide variety of noble-metal halides.

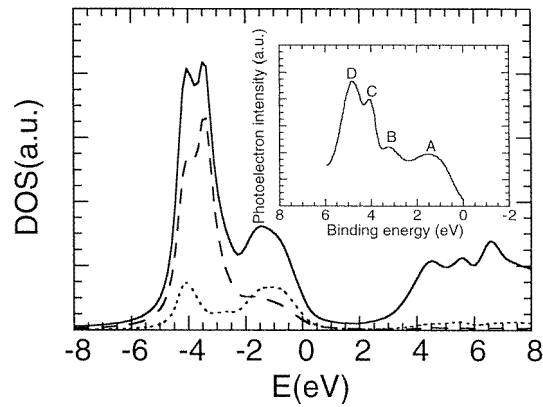


Figure 7. Theoretical densities of states for γ -AgI. The solid curve stands for the total density of states; the broken and dotted curves stand for the partial components arising from the Ag d and I p states, respectively. The inset shows the photoemission result obtained by Goldmann *et al* [7, 8]. The energies are measured with reference to the Fermi level.

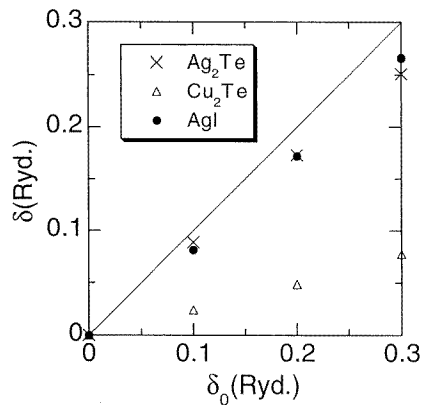


Figure 8. The actual shift δ versus the given shift δ_0 of the selective band for Ag_2Te , Cu_2Te and AgI.

To elucidate the strength of coupling between the d and p bands in the noble-metal compounds, we have utilized vitally the APW method in which the APW basis functions have a definite quantum number for the angular momentum inside each MT sphere. That is, we selectively shifted downward the d band originating from the Ag d states in Ag_2Te and AgI or the p band from the Te p states in Cu_2Te . Figure 8 shows the actual shift δ as a function of the given shift δ_0 of the selective band for the three compounds. In Ag_2Te and AgI, the two bands are so easily separable that the Ag d states preserve their localized nature during the hybridization. On the other hand, Cu_2Te gives rise to strong admixture of the Cu d states and the Te p states. The resulting band structures for AgI, Ag_2Te and Cu_2Te with $\delta_0 = 0.3$ Ryd are shown in the panels (b) of figure 6 and figure 9; the structure of the d band in Cu_2Te is substantially modified by such a procedure as expected. The difference between Cu and Ag ions as regards their diffusivity in the tellurium cage can thus be traced back to the very different degrees of p-d hybridization taking place in the compounds.

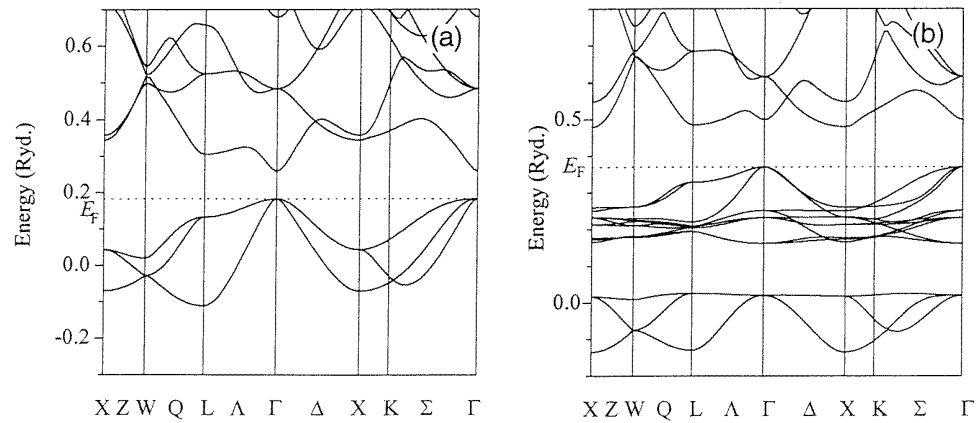


Figure 9. As figure 4, but recalculated by selectively lowering the d band for Ag_2Te or the p band for Cu_2Te by 0.3 Ryd.

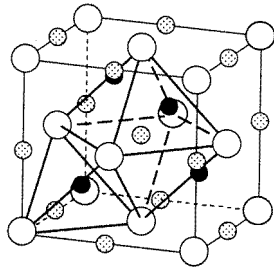


Figure 10. The crystal structure with space group $F\bar{4}3m$, adopted as a transition state for ionic diffusion in the tellurides. The white spheres stand for Te atoms forming an FCC sublattice; the black and grey spheres stand for mobile cations located at the tetrahedral and octahedral sites, respectively.

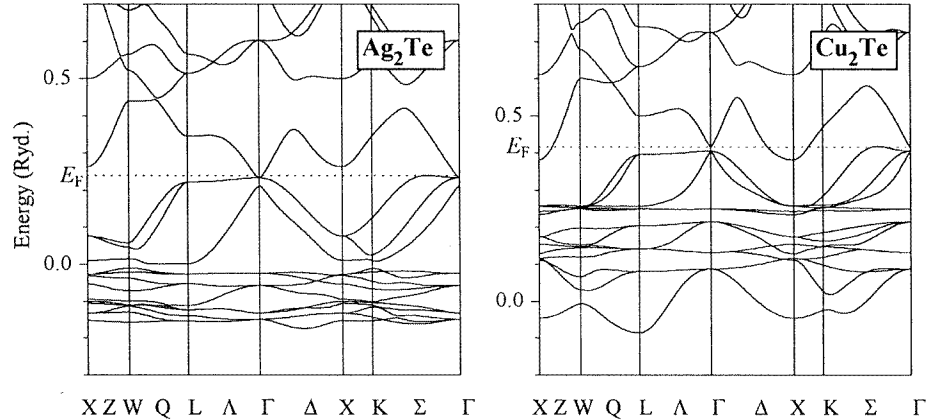


Figure 11. Band structures of Ag_2Te and Cu_2Te with the $F\bar{4}3m$ structure, calculated at the equilibrium lattice constants. From reference [24].

5. Effects of ionic diffusion on the electronic structure

We finally investigate how the electronic structure of Ag_2Te depends on the silver diffusion, along with making an estimation of the associated activation energy. Combination of the

diffraction experiments [25, 26] and the MD simulations [35] reveals that the Ag ions migrate among the tetrahedral sites via the octahedral sites. This observation led us to adopt the antifluorite structure as the ground state and the crystal structure with the space group $F\bar{4}3m$ (see figure 10) as a transition state in the diffusion process of the Ag ions. The actual degree of disorder in α -Ag₂Te may be overemphasized in this choice of the transition state, in which Ag atoms are distributed evenly on the tetrahedral and octahedral sites. Figure 11 shows the band structure of such activated Ag₂Te, accompanied by that of Cu₂Te with the same structure. The scattered distribution of Ag exerts no significant influence on the electronic structure of the ground state already given in figure 4. This confirms again the weak coupling between the Ag d states and the Te p states in Ag₂Te. In contrast, the band structure of Cu₂Te sensitively depends on the location of Cu ions; this is reminiscent of the strong p–d hybridization in Cu₂Te.

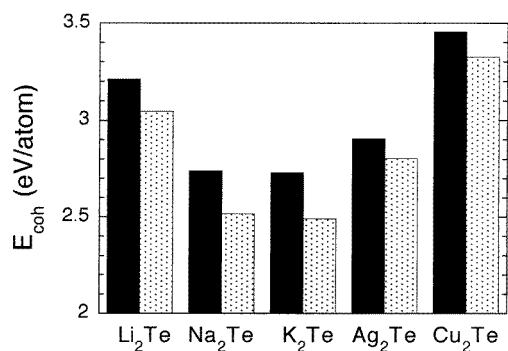


Figure 12. Cohesive energies per atom for various tellurides in eV. The solid and dotted bars show the results calculated with the $Fm\bar{3}m$ and $F\bar{4}3m$ structures, respectively.

Figure 12 shows the cohesive energies of all of the tellurides studied here with the $Fm\bar{3}m$ and $F\bar{4}3m$ structures. We calculated the activation energy by taking the difference between the cohesive energies of the ground and transition states and assuming that it amounts to the energy difference per mobile cation. The activation energy in Ag₂Te is experimentally estimated as 0.1–0.2 eV [18], which is in good agreement with the theoretical value so calculated, 0.153 eV. The predicted activation energy, 0.197 eV, for Cu₂Te is appreciably larger than that for Ag₂Te. It also compares favourably with the value, 0.2 eV, extracted from the experimental results for the high-temperature phase of Cu₂Te, No 2, given in [17]. The calculated activation energies for Li₂Te, Na₂Te and K₂Te are 0.251, 0.335 and 0.357, respectively, in eV. These results for the alkali tellurides are ordered in accordance with the size of the cations.

6. Conclusion

Fully self-consistent LAPW calculations have been carried out for various tellurides with the antifluorite structure. We paid attention to the difference between the closed-shell structures of the noble-metal and the alkali ions embedded in the Te sublattice; the noble-metal ions with the closed d shells are remarkably deformable. Taking advantage of the APW method we measured the strength of the p–d hybridization in Ag₂Te and Cu₂Te. Such a measurement clearly distinguishes these two compounds; the d band is much more tightly coupled with the p band in Cu₂Te. The activation energies for the cation diffusion in the tellurides were evaluated and the trend of the ionic diffusivity predicted from their magnitudes is in harmony with the observations. Compiling these results we conclude that the fast diffusivity of Ag ions is primarily ascribable to flexibility in the variation of their

charge distribution dominated by deformation of the *isolated* d electrons; the isolated nature of the d states arises from the weakness of the p–d hybridization. We have also applied the LAPW calculation to γ -AgI and obtained firm support for the conclusion.

Acknowledgments

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