Electronic Structure of the Chevrel-Phase Compounds Sn$_{x}$Mo$_{6}$Se$_{7.5}$: Photoemission Spectroscopy and Band-structure Calculations

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We have studied the electronic structure of two Chevrel-phase compounds, Mo$_{6}$Se$_{7.5}$ and Sn$_{1.2}$Mo$_{6}$Se$_{7.5}$, by combining photoemission spectroscopy and band-structure calculations. Core-level spectra taken with x-ray photoemission spectroscopy show systematic core-level shifts, which do not obey a simple rigid-band model. The inverse photoemission spectra imply the existence of an energy gap located $\sim$ 1 eV above the Fermi level, which is a characteristic feature of the electronic structure of the Chevrel compounds. Quantitative comparison between the photoemission spectra and the band-structure calculations have been made. While good agreement between theory and experiment in the wide energy range was obtained as already reported in previous studies, we found that the high density of states near the Fermi level predicted theoretically due to the Van Hove singularity is considerably reduced in the experimental spectra taken with higher energy resolution than in the previous reports. Possible origins are proposed to explain this observation.

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I. INTRODUCTION

The Chevrel-phase compounds, which have been extensively studied in the 1970’s as one of the largest families of superconductors, have recently invoked renewed interest as a candidate for new thermoelectric materials. Their general formula is $A_xMo_6X_8$, where $X$ stands for a chalcogen atom, namely, S, Se, or Te and $A$ atom is an alkali metal, alkaline earth, simple metal, transition metal, noble metal, or rare earth. Up to now, dozens of compounds with this formula are known, a large portion of which show superconductivity. Crystallographically, they have a rather remarkable structure consisting of Mo$_6$X$_8$ clusters. In this sense, the Chevrel system is a forerunner of cluster-based superconductors like the fullerene. Such materials tend to have rather exotic electronic structures, which gives us a unique opportunity to search for new compounds with novel properties.

Theoretically, a number of band-structure calculations have been reported for the Chevrel-phase compounds. Two characteristic features should be remarked. The first is the high density of states (DOS) near the Fermi level ($E_F$) mainly due to flat bands of Mo 4$d$ character, which would favor a high superconducting transition temperature according to standard BCS theory. In fact, the Fermi level is located close to a Van Hove singularity (VHS). In addition, the flat bands mean a low Fermi velocity, which leads to a short coherence length and hence a high critical magnetic field ($H_{c2}$).

Second, there exists an energy-gap-like structure about 1 eV above $E_F$. This arises from a splitting between the bonding and anti-bonding states of the Mo 4$d$ manifold and its position relative to $E_F$ depends on the number of electrons in the cluster. It is this feature as well as the cluster-based crystal structure that gives some researchers the hope that there may exist new thermoelectric materials among the Chevrel-phase compounds.

Experimentally, photoemission spectroscopy (PES) is one of the most useful methods to investigate the electronic structures, and it has already been applied to this system several times. Following the earlier work by Ihara and Kimura, many studies have been reported including x-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS) and x-ray emission spectroscopy. Although the measured valence-band spectra were compared with band-structure calculations and good agreement was obtained between experiment and theory, the experiment has not been performed using high enough resolution in order to access the electronic structure near $E_F$. The information about the unoccupied states to be measured by inverse photoemission spectroscopy (IPES) has also been lacking.

In this paper, we will report on a study of the electronic
structure of two Chevrel-phase compounds, Mo$_6$Se$_7$ and Sn$_{1.2}$Mo$_6$Se$_7$, combining the results of PES, IPES, and the band-structure calculations. First, the experimental results of the core-level, valence-band, and conduction-band spectra will be shown. The valence-band spectra were taken with much higher resolution than in previous reports. Second, after the results of the band-structure calculations for Mo$_6$Se$_7$ and SnMo$_6$Se$_8$ are reported, quantitative comparison between the experimental PES and IPES spectra and the theoretical spectra derived from the band-structure calculations will be performed. We finally discuss to which extent the theory explains the experimental results.

II. EXPERIMENT

A. Sample Preparation

Polycrystalline samples of Mo$_6$Se$_7$ and Sn$_{1.2}$Mo$_6$Se$_7$ were prepared as follows. For Mo$_6$Se$_7$, a mixture of Mo and Se with the desired ratio was sealed in an evacuated silica tube, and was then heated from 200°C to 900°C in a rate of 100°C/hour, followed by annealing at 900°C for 12 hours. The product was ground and pressed into a pellet, and was then annealed at 1200°C for three days. For Sn$_{1.2}$Mo$_6$Se$_7$, a mixture of the desired ratio of Sn, Mo and Se powders was heated in an evacuated silica tube at 200°C for 12 hours and 250°C for 12 hours, and was then heated up to 800°C in a rate of 100°C/hour, followed by annealing at 800°C for 24 hours. The product was pressed into a pellet and was annealed again at 1000°C for a week. X-ray diffraction patterns of both samples were successfully indexed on the basis of the Chevrel structure. The hexagonal lattice parameters were determined to be $a = 9.568$ Å and $9.521$ Å and $c = 11.180$ Å and $11.838$ Å for Mo$_6$Se$_7$ and Sn$_{1.2}$Mo$_6$Se$_7$, respectively. The Sn$_x$Mo$_6$Se$_8$ phases were stabilized when the atomic ratio between Mo and Se was slightly non-stoichiometric. While the x-ray diffraction does not show any extra phase caused by the non-stoichiometry, it is not known whether Se deficiency or excess Mo is responsible for this non-stoichiometry. Judging from the result for the sulfide Chevrel-phase compound, however, the former is more likely than the latter. Transitions to the superconducting states were found to occur at 5–8 K for Mo$_6$Se$_7$ and 2–8 K for Sn$_{1.2}$Mo$_6$Se$_7$, being consistent with previous reports.

B. Photoemission Measurements

The XPS measurements were done using the Mg Kα line ($h\nu = 1253.6$ eV) and photoelectrons were collected using a PHI double-pass cylindrical-mirror analyzer. The UPS measurements were made using the He I and He II resonance lines ($h\nu = 21.2$ eV and 40.8 eV, respectively) and a VSW hemi-spherical analyzer. The IPES or Bremsstrahlung-isochromat spectroscopy (BIS) measurements were performed by detecting photons of $h\nu = 1486.6$ eV using a quartz monochromator. The XPS and BIS measurements were made at liquid-nitrogen temperature, and the UPS measurements at ~ 28 K. We did the energy calibration and the estimation of the instrumental resolution by using Au evaporated on the surface of the samples after each measurement. They were performed for XPS by defining Au 4$f_7/2 = 84.0$ eV, and for UPS and BIS by measuring the Fermi edge. The total resolution was ~ 1 eV, ~ 35 meV, ~ 80 meV, and ~ 1 eV for XPS, He I UPS, He II UPS, and BIS, respectively.

The samples were scraped in situ with a diamond file in every measurement. During the XPS measurements, the intensity of the O 1s core-level signal, which indicates contaminations on the sample surfaces, did not increase for several hours, once it had been almost removed. Therefore, the measurements of XPS and BIS were undertaken by scraping the samples every several hours. Scraping was, however, done more frequently for the UPS measurements because UPS is more surface-sensitive than XPS and BIS.

III. EXPERIMENTAL RESULTS

A. Core-level Spectra

Figures 1 (a), (b), (c), and (d) show the Mo 3$p$, Mo 3$d$, Se 3$p$, and Se 3$d$ core-level spectra of Mo$_6$Se$_7$ and Sn$_{1.2}$Mo$_6$Se$_7$ obtained by XPS, respectively. The horizontal axis ($E$) measures the energy relative to $E_F$ and the binding energy ($E_B$) is given by $-E$. Two observations are worth mentioning. First, systematic core-level shifts occur in going from Mo$_6$Se$_7$ to Sn$_{1.2}$Mo$_6$Se$_7$. Second, the lineshape of the Mo core level looks more asymmetric with longer tail towards higher binding energy than that of the Se core level. This is a feature common in both compounds.

To be more quantitative on those points, we made a lineshape analysis by means of the least-square fitting. It is assumed that each core-level peak has Mahan’s asymmetric lineshape reflecting the effect of core-hole screening by conduction electrons in metals. The degree of asymmetry is characterized by the singularity index $\alpha$ given by

$$\alpha = 2 \sum_l (2l + 1) (\delta_l^2 + 1) = \sum_l \frac{q_l^2}{2(2l + 1)},$$

where $q_l$ is the charge of the conduction electrons with angular momentum $l$ which screens the core hole and $\delta_l$ is the phase shift, satisfying Friedel’s sum rule $\sum_l q_l = 1$. The lineshape is convoluted with a Gaussian and a Lorentzian function which represent the instrumental
resolution and the core-hole lifetime broadening, respectively. The integral background is also assumed. The lineshape analysis could be successfully made except for the Mo 3d core-level spectra which contain the weak Se 3s core-level peak at \( E \sim -229 \) eV. The results are shown for the Mo 3p, Se 3p, and Se 3d core-level spectra of both compounds in Figs. (a), (c), and (d) by solid curves, respectively. The fitted parameters are shown in Table I.

TABLE I. Core-level peak position \( E \) and singularity index \( \alpha \) obtained by the lineshape analysis. Only for the Mo 3d core level, the peak positions determined by their intensity maxima are listed. \( \Delta E \) denotes the spin-orbit splitting between \( 3p_{3/2} \) and \( 3p_{1/2} \) or between \( 3d_{5/2} \) and \( 3d_{3/2} \).

| Core Level | \( E \) (eV) | \( \Delta E \) (eV) | \( \alpha \) | \( E \) (eV) | \( \Delta E \) (eV) | \( \alpha \) |
|------------|-------------|----------------|-----|-------------|----------------|-----|
| Mo 3p\( _{3/2} \) | -393.67 | 17.52 | \sim 0.18 | -393.67 | 17.52 | \sim 0.18 |
| Mo 3d\( _{5/2} \) | -228.03 | 3.13 | - | -227.88 | 3.14 | - |
| Se 3p\( _{3/2} \) | -160.38 | 5.77 | \< 0.02 | -160.27 | 5.77 | \< 0.01 |
| Se 3d\( _{5/2} \) | -53.91 | 0.91 | \sim 0.05 | -53.78 | 0.88 | \sim 0.07 |

First of all, it is found from Table I that the singularity indices of the Mo core levels are larger than those of the Se core levels, in qualitative agreement with the result of the sulfide Chevrel-phase compound. This observation indicates that the contribution from the Mo 4\( d \) electrons is dominant at \( E_F \) rather than that from Se 4\( p \), being qualitatively consistent with the band-structure calculations. Secondly, we also found that each core level in Mo\( \_6 \)Se\( \_7.5 \) is located at a binding energy which is 0.1–0.2 eV higher than that in Sn\( \_1.2 \)Mo\( \_6 \)Se\( \_7.5 \). As for the trend of the core-level shifts, it was reported that the shifts have weak linear correlation with the inter-cluster Mo-Mo distance and the rhombohedral lattice parameter of the Chevrel systems judging from the core-level and Mo 1s absorption spectra of various \( A_2M_6X_8 \) compounds (\( A = \text{Pb}, \text{Ni}, \text{Cu} \), and so on and \( X = \text{S}, \text{Se}, \text{and Te} \)). Our results follow the same trend in that \( E_B \) increases as the Mo-Mo distance increases. Since the total number of electrons in the cluster increases when Sn is added to Mo\( \_6 \)Se\( \_7.5 \), the rigid band model predicts that each core-level binding energy should increase in going from Mo\( \_6 \)Se\( \_7.5 \) to Sn\( \_1.2 \)Mo\( \_6 \)Se\( \_7.5 \). The observed core level shifts are therefore opposite to those expected from the rigid-band model that Sn is an electron donor and that the Fermi level would be raised by Sn-doping. Thus, our results imply that the valence band structure itself changes and the system behaves unlike a rigid band model when Sn is added interstitially to Mo\( \_6 \)Se\( \_7.5 \).

B. Valence-band Photoemission Spectra

The valence-band XPS and UPS spectra of Mo\( \_6 \)Se\( \_7.5 \) and Sn\( \_1.2 \)Mo\( \_6 \)Se\( \_7.5 \) in the entire valence band and in the vicinity of \( E_F \) are shown in Figs. (a) and (b), respectively. They have been normalized to the area of the whole valence band which spreads between \( E \sim -8 \) eV and 0 eV after the background of integral type and Henrich type had been subtracted for the XPS and UPS spectra, respectively.

Roughly speaking, three structures are identified in the spectra of both compounds. For the moment, these structures are referred to as A (from 0 to \( E \sim -2 \) eV), B (\( E \sim -3 \) eV), and C (from \( E \sim -4 \) to \( E \sim -7 \) eV) as indicated in the figure. Because the Sn 5s core level is observed at \( E \sim -14 \) eV, we have to take into account only Mo 4\( d \) and Se 4\( p \). The contribution of Mo 5\( s \) and Sn 5\( p \) to the valence-band spectra is negligible because of their small numbers of electrons in these compounds and of their relatively small cross-sections. Based on the fact that the relative cross-sections of Se 4\( p \) to Mo 4\( d \) is largest at \( h\nu = 1253.6 \) eV (XPS) and smallest at 40.8 eV (He II UPS), we can consider A to be of mainly Mo 4\( d \) character which shows up as a distinct peak in the He I and He II UPS spectra. In a similar way, structures B and C are attributed to Se 4\( p \) character because they appear as strong broad features in XPS. In the UPS spectra, it is hard to discriminate between B and C because of the low energy resolution. The above assignment is qualitatively consistent with the band-structure calculations.
(see Fig. 4): Mo 4d character is dominant in the rather narrow energy range from $E = 0$ to $-2$ eV and Se 4p character appears as a broad band from $E \sim -3$ to $-7$ eV. Quantitative comparison will be made below.

The intensity between $E = -0.3$ and $-1.2$ eV of Sn$_{1.2}$Mo$_6$Se$_{7.5}$ is higher than that of Mo$_6$Se$_{7.5}$, which holds true for all the three spectra as seen in Fig. 2(b). Here, it may be tempting to consider that the Mo 4d band of Mo$_6$Se$_{7.5}$ is shifted by $\sim 0.3$ eV to higher binding energy compared with that of Sn$_{1.2}$Mo$_6$Se$_{7.5}$, corresponding to the core-level shift. We should, however, emphasize again that the rigid-band model predicts the opposite. Indeed, the lineshape around $E_F$ is qualitatively different between both compounds, which clearly means that a simple rigid-band model is not applicable to the Chevrel system and that the insertion of Sn atoms between the clusters certainly change the electronic structure around $E_F$. Alternatively, the shift can be partly attributed to the narrowing of the Mo 4d band due to the increase in the distance between the Mo$_6$Se$_{7.5}$ clusters. Generally, when the X atom in the Mo$_6$X$_8$ cluster goes from S to Se, the lattice parameters increase due to a larger atomic radius of Se. In a similar way, by inserting large atoms such as Sn and Pb, the distance between the clusters increases. This results in the decrease of the Mo 4d bandwidth, and in turn lowers the position of $E_F$ relative to the other core and valence levels because the Fermi level is located close to the top of the Mo 4d band in the bonding states. Actually, a slight decrease of the Mo 4d band width from Mo$_6$Se$_{7.5}$ to SnMo$_6$Se$_{8}$ is also predicted in the band-structure calculations as reported below.

C. BIS Spectra

The BIS spectra of Sn$_{1.2}$Mo$_6$Se$_{7.5}$ and Mo$_6$Se$_{7.5}$ are shown in Fig. 3 with closed and open circles, respectively. The BIS spectrum of Au near the Fermi level is also shown in the top panel of the figure for the sake of comparison. The main peak at $E \sim 2$ eV is readily assigned to Mo 4d character, namely the antibonding states of the Mo 4d band, because Mo 4d has a high density of unoccupied states and its cross-section is larger than the other components such as Se 4p. The broad structure at $E \gtrsim 6$ eV is of Mo 4p character. As marked in Fig. 3, the main peak position of Sn$_{1.2}$Mo$_6$Se$_{7.5}$ is shifted to higher energy relative to that of Mo$_6$Se$_{7.5}$ by $\sim 0.35$ eV. This shift and its direction are consistent with the PES results, which is explained in the same way as above: in going from Mo$_6$Se$_{7.5}$ to Sn$_{1.2}$Mo$_6$Se$_{7.5}$, the narrowing of the Mo 4d bands occurs not only in the bonding state but also in the antibonding state and the position of $E_F$ is lowered relative to the core levels. On the other hand, the centroid of the band in both states should be unaffected by the narrowing in the first approximation, making the Mo 4d peak in the unoccupied state shifted away from $E_F$ in the Sn$_{1.2}$Mo$_6$Se$_{7.5}$ spectra.

Now, a characteristic feature in Fig. 3 is the existence of a shoulder at $E \sim 0.5$ eV in the Sn$_{1.2}$Mo$_6$Se$_{7.5}$ spectrum as marked by an arrow in the figure. This shoulder implies the existence of a dip in the unoccupied DOS. Though not so obvious as in the Sn$_{1.2}$Mo$_6$Se$_{7.5}$ spectrum, there is a similar shoulder at $E \sim 1$ eV in the Mo$_6$Se$_{7.5}$ spectrum. As mentioned above, the band-structure calculations for many Chevrel-phase compounds have predicted the existence of an energy gap around 1 eV above $E_F$. The observed shoulder is consistent with this considering the $\sim 1$ eV energy resolution of the BIS measurements [see Fig. 3(a)]. To the best of our knowledge, the above observation is the first experimental indication of the existence of the gap above $E_F$ in the Chevrel-phase
compounds.

![BIS spectra](image)

**FIG. 3.** BIS spectra of $\text{Sn}_{1.2}\text{Mo}_6\text{Se}_{7.5}$ and $\text{Mo}_6\text{Se}_{7.5}$. The arrows indicate the shoulder around 1 eV above $E_F$. In the top panel, the spectrum of gold is also plotted.

### IV. BAND-STRUCTURE CALCULATIONS

In order to interpret the experimental results from a theoretical viewpoint, we have performed band structure calculations for both compounds. The band structure was calculated self-consistently using the local density-functional approximation (LDA) and the scalar relativistic linear muffin tin orbital method (LMTO) in the atomic sphere approximation (ASA) including the combined correction (CC). In the ASA+CC, the one-electron potential entering the Schrödinger's equation is a superposition of overlapping spherical potential wells with a position $R$ and radii $s_R$, plus a kinetic energy error proportional to the fourth power of the relative overlap of the spheres. The radii of the overlapping muffin-tin spheres are determined by the following conditions, that the overlapping muffin-tin potential be the best possible approximation to the full potential, and that the error due to sphere overlap be acceptable. For the Chevrel phases with open structure, these conditions cannot be achieved only with atom centered spheres so several interstitial (empty) spheres were included to achieve good sphere packing and an overall good representation of the potential. The radii of the atomic and the interstitial spheres as well as the position of the interstitial spheres were calculated by using an automatic procedure developed by Krier et al. In the present calculation we allowed an overlap of 16 percent between atom centered spheres, 18 percent between atom centered and the interstitial spheres and 20 percent between the interstitial spheres.

The basis set for both the compounds consisted of Mo 5$s$, 5$p$, 4$d$; Se 4$p$ and the interstitial 4$s$ LMTO’s. In addition for $\text{SnMo}_6\text{Se}_8$ we included Sn 5$s$, 5$p$ LMTO’s. Se 4$s$, 4$d$; Sn 4$d$ and interstitial 4$p$ were downfolded. This treatment not only reduced the size of the secular matrix but also avoided distortions of the phase shift of the high partial waves. Such distortions or even ghost bands, may occur with the conventional LMTO method. All $k$-space integrations were performed by the tetrahedron method using 254 irreducible $k$-points within the Brillouin zone.

The calculated density of states (DOS) are shown in Figs. 4 (a) and (b) for $\text{SnMo}_6\text{Se}_8$ and $\text{Mo}_6\text{Se}_8$, respectively, and they are consistent with the previous reports on other Chevrel-phase compounds. The DOS at $E_F$ is very high and situated near the VHS, which explains the asymmetric lineshape of the Mo core-level spectra. The width of the Mo 4$d$ band in the bonding states decreases from 6.4 eV to 5.7 eV in going from $\text{Mo}_6\text{Se}_8$ to $\text{SnMo}_6\text{Se}_8$, which may be partly responsible for the aforementioned non-rigid-band-like behavior. It should be noted here that the role of the insertion of Sn atoms between the clusters is to change not only the number of electrons but also the cluster-cluster interactions.

![Calculated DOS](image)

**FIG. 4.** Calculated DOS of (a) $\text{SnMo}_6\text{Se}_8$ and (b) $\text{Mo}_6\text{Se}_8$, with the total DOS and Mo 4$d$ partial DOS shown by the solid line and the shaded area, respectively.

### V. COMPARISON BETWEEN THEORY AND EXPERIMENT

In this section, we will make a quantitative comparison between the photoemission spectra and theoretical spec-
In spite of that agreement, however, there exists a large discrepancy just around \( E_F \) between the experimental and theoretical He II spectra as shown in Fig. 5 (b): while the intensity of the Mo\(_{6}\)Se\(_{7.5}\) spectra is larger than that of the Sn\(_{1.2}\)Mo\(_{6}\)Se\(_{7.5}\) spectra, which qualitatively holds true in theory and experiment, the absolute intensity is not reproduced at all. Indeed, the sharp peak in the theoretical spectra originating from the VHS completely disappears in the experimental spectra. Although the energy resolution is not high enough to check this point for the BIS spectra, one can see a similar tendency in the BIS spectra, too. We believe that the disappearance of the VHS is intrinsic judging from the overall good agreement between theory and experiment in the wide energy range. Actually, there are several effects which have been neglected in the band-structure calculations. The remarkable reduction of the PES intensity near \( E_F \) indicates that such an effect plays a significant role in the spectra on the low energy scale. Because the total spectral weight should be conserved if integrated to a sufficiently high energy, the significant weight near \( E_F \) which is theoretically predicted is supposed to be transferred to the region away from \( E_F \) (at least 1–2 eV from \( E_F \)) in the experimental spectra. Similar discrepancy between theory and experiment exists in the photoemission spectra of another cluster-based superconductor K\(_3\)C\(_6\)O\(_6\).

Several candidates which can cause the above phenomenon may be listed. Firstly, disorder due to the non-stoichiometry. The Se deficiency (and the excess of Sn for Sn\(_{1.2}\)Mo\(_{6}\)Se\(_{7.5}\)) may create a random potential which reduces the coherence of the electrons, leading to the decrease of the spectral intensity near \( E_F \). It has been reported that static disorder causes such an
effect in the PES spectra of TaSe$_2$. A PES study for more stoichiometric single crystals of Chevrel-phase compounds will clarify this point. Secondly, we may consider electron-phonon interactions. It was reported that the electron-phonon coupling constant ($\lambda$) in the Chevrel-phase compound is as large as $\sim 1$ (Ref. 3), a value which may reduce the spectral intensity to almost half of the theoretical value. The same explanation has been made for K$_2$CuF$_4$. The typical energy of phonons in the Chevrel-phase compounds is, however, only $\sim 10$ meV (Ref. 3), which cannot cause the transfer of spectral weight. An indication of the energy gap located above the Fermi level characteristic of the Chevrel system was obtained in the BIS spectra. We have also calculated the band-structure of Mo$_6$Se$_8$ using PES experiment and band-structure calculations. The overall good agreement between theory and experiment in the wide energy range shows that the LDA is valid for these compounds.

The flexibility of the insertion of cations into the unique cluster-based structure is attractive and, besides the possibility of application as thermoelectric materials, there may lie new aspects in the Chevrel-phase and related compounds such as one-dimensional compounds made of Chevrel clusters. Systematic theoretical and experimental studies are needed to clarify the relationship between the inserted atoms and the electronic structures around $E_F$. Such information would be useful to finely tune the electronic properties of the Chevrel-phase compounds.

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**VI. CONCLUSION**

We have studied the electronic structure of two Chevrel-phase compounds, Mo$_6$Se$_7.5$ and Sn$_{1.2}$Mo$_6$Se$_{7.5}$, using PES experiment and band-structure calculations. The XPS core-level spectra have revealed systematic shifts, for which the change of the Mo-Mo inter-cluster distances may be responsible. From the fact that the valence-band spectra do not agree with the rigid-band model, we propose that the narrowing of the Mo 4$d$ bands caused by the insertion of Sn atoms explains the observed shift. An indication of the energy gap located $\sim 1$ eV above the Fermi level characteristic of the Chevrel system was obtained in the BIS spectra. We have also calculated the band-structure of Mo$_6$Se$_8$ and SnMo$_6$Se$_8$ and compared them with the experiment. The overall good agreement between theory and experiment in the wide energy range shows that the LDA is valid for these compounds. On the other hand, the high DOS due to the VHS was reduced in the experimental spectra. While it has been reported several times that band-structure calculations reproduce well the experimental valence band spectra, such a discrepancy was first found in the present study because of higher energy resolution than the previous work.

Our results imply that the insertion of various atoms between the clusters influences the electronic structure around $E_F$ through a change in the inter-cluster interaction resulting in the change beyond the simple rigid-band picture. The flexibility of the insertion of cations into the unique cluster-based structure is attractive and, besides the possibility of application as thermoelectric materials, there may lie new aspects in the Chevrel-phase and related compounds such as one-dimensional compounds made of Chevrel clusters. Systematic theoretical and experimental studies are needed to clarify the relationship between the inserted atoms and the electronic structures around $E_F$. Such information would be useful to finely tune the electronic properties of the Chevrel-phase compounds.

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