Soft x-ray photoelectron spectroscopy study of type-I clathrates

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Abstract

Extensive soft x-ray photoelectron spectroscopy studies are performed on Ba₈Ga₁₆Ge₃₀ (BGG) and Sr₈Ga₁₆Ge₃₀ (SGG) single crystals ranging from Fermi to core levels, at a high-energy facility. Valence band x-ray photoelectron spectroscopy (XPS) experiments with theoretical calculations revealed that the valence band is mainly constructed by the Ge/4s and 4p wave functions with little contribution of the Ba/Sr atomic orbitals. Surprisingly, unexpected features evidencing the different shift for the 2a- and 6d- sites between Ba 4d and Sr 3d are observed. The detailed analyses including theoretical support by first-principles band-structure calculations lead to the conclusion that the component distributions of the larger tetrakaidecahedral cage are different depending on the endohedral atoms, which contrasts with the past consensus that BGG and SGG have the same framework structure. This may give thorough reconsiderations on earlier interpretations of experimental data.

Keywords: thermoelectric, synchrotron radiation, x-ray photoelectron spectroscopy, valence band, core level

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Thermoelectric materials have been attracting intense research interest because the conversion from thermal to electric energy is a very promising alternative to solve the energy resource problems in this century. For this purpose, many materials have been searched to date, such as degenerate semiconductors, half-Heusler alloys, heavy fermion compounds, cobalt oxides and so forth [1–5]. A new concept (phonon glass and electron crystal (PGEC)) was introduced by Slack in 1995 [6], which has been used as one of the most useful design methods for power generation materials. In the PGEC concept, heat transfer is suppressed by phonon scattering, even though electric transport remains high due to the periodic regulations in the lattice, which then gives rise to high thermoelectric figure of merit \( ZT = TS^2\sigma/\kappa \) (where \( S \) denotes the Seebeck coefficient, \( T \) is temperature, \( \sigma \) is the electric conductivity, and \( \kappa \) is the thermal conductivity) and consequently higher energy conversion efficiency. Host–guest type materials such as clathrates have been studied as very promising candidates along this concept. Such demonstrations of low \( \kappa \) and simultaneously high \( TS^2\sigma \)
Figure 1. Structure of type-I clathrates. There are two accommodation sites for endohedral atoms, denoted by 2a and 6d, and the 6d large inner space affords the freedom of motion especially for smaller atomic elements. A schematic rattling model in the 6d-site under the created potentials is also shown inside the cage in the lower part of the right figure.

have recently been reported for type I clathrates, M₈Ga₁₆Ge₃₀ (M = Ba : BGG, M = Sr : SGG and M = Eu : EGG) [7, 8], and applications are already under consideration due to the observed high energy conversion efficiency [9].

The energetics of the endohedral atoms, confined under the potentials created by the surrounding spaces, is very important, especially for the PGEC concept. Rattling phonons have been proposed as the key issue, ever since elastic neutron diffraction studies in M₈Ga₁₆Ge₃₀ demonstrated that the smaller-size Sr atom shows a wider distribution of its density map than that of the larger-size Ba, while the Eu atom shows an even wider quartic density distribution [8]. More recent Mössbauer experiments have demonstrated that the endohedral Eu atoms in EGG display rattling motions with a quantum tunneling mode from the viewpoint of the loss in hyperfine structure [10]. Raman spectroscopy has also shown unusual temperature dependences of the vibration modes in this clathrate family [11], and a dominant thermal-mode rattling is suggested above 2 K. Typical type-I clathrates have cubic structure belonging to space group Pm₃n (No. 223). The unit cell of the host framework consists of two dodecahedral and six larger tetrakaidecahedral cages; see figure 1. Although many experiments, such as heat capacity, thermal transport, x-ray diffraction (XRD) and temperature-dependent inelastic neutron scattering [8, 12–14], have been applied to elucidate the real nature of these materials, debates for whether the rattler or the framework plays an important role still continues.

In this paper, energetics of type-I clathrates BGG and SGG, including the valence band, Ba 4p/4d, Sr 3p/3d and Ga 3d core levels, as well as the theoretical models, are investigated by employing soft x-ray photoelectron spectroscopy (XPS) at a synchrotron radiation facility. In addition, the resonance experiments of Ba (3d to 4f transition) excitation have been carried out by varying the irradiation energy from 750 to 800 eV. These results strongly suggest that the outer cage structure changes depending on the types of endohedral atoms, and that the rattling phonons discussed in previous studies are created under the local anharmonic potentials. We think that these important factors should be considered in order to understand the rattling phonons in this system as well as to design higher-performance thermoelectric materials.

2. DOS at valence states

Single crystals of BGG and SGG were prepared according to the Ga self-flux method as described in a recent paper [14]. Their structure was confirmed by x-ray diffraction (XRD). All the observed peaks can well be indexed using Pm₃n space group for both BGG and SGG samples, and the samples were of very high quality. However, XRD cannot confirm whether or not the framework is homogeneous because the atomic scattering factors are very close between Ga and Ge. Inductively coupled plasma analyses showed that smaller stoichiometry of Ga than Ba gives n-type semiconducting character in these materials.

Soft x-rays are an effective probe for observing bulk electronic states compared with ultraviolet light, because of the long photoelectron mean free path from the surface. The valence band XPS spectra of n-type BGG have been measured with the incident x-ray energy of 776 eV as shown in figure 2,
Figure 3. Soft x-ray photoelectron spectra of the valence states and theoretical band structure in SGG. The inset is the expanded view around the Fermi level.

where the Fermi level is set to zero. From the XPS spectrum, three bands are clearly observed at energies ranging from 0 to 12 eV. The band structure of BGG calculated using the WIEN2k code [15] is added for comparison. Electronic states of BGG and SGG were calculated by the full potential linearized augmented plane wave (FLAPW) method with the generalized gradient approximation (GGA). The guest atoms were put in high-symmetry positions for both kinds of sites. The details have been reported elsewhere [16].

Comparison of the experimental results to calculation reveals that these three bands are mainly constructed by the Ge/Ga 4s and 4p wave functions with little contribution of the Ba 5s, 5p and 5d ones. We can clearly see that the band gap is opened. Supposing that the Fermi level is located in the middle between the conduction band and the valence band, the band gap \( \Delta E_g \) can be estimated as 1.4 eV.

The valence band spectrum of SGG shows a similar structure to that of BGG, as shown in figure 3. The valence band consists of three bands and the band gap is also opened by \( \Delta E_g = 1.6 \) eV. In the present experiments, the band gap is not much different between BGG and SGG. However, both previous band calculations and our calculations show that SGG has a smaller band gap than BGG [17], and this is not consistent with our experimental results. We presume that the carriers existing in our samples may cause this difference, since the band calculations are made supposing the ideal stoichiometry.

3. Ba 3d resonance

Resonance experiments of the valence band are useful in order to see what kinds of orbitals are involved in constructing the valence band. For Ba encapsulated clathrates, the present study used Ba 3d resonance with on- and off- modes with the excitation of Ba 3d to 4f levels in order to investigate wave functions for constructing the Fermi surface, as discussed in the previous studies on type-I clathrate Ba\(_8\)Si\(_{46}\) and type-III clathrate Ba\(_2\)Ge\(_{100}\) [18, 19]. The resonance spectroscopy of BGG has been performed, as shown in figure 4. The intensity of the first valence band near the Fermi level was modified, but its change was small. This indicates that the Ba orbitals, most likely 4d, 5s and 5p, have little contribution to the reconstruction of the valence band. This is consistent with characters of the wave functions of the valence band assigned by calculations as described in the previous paragraph.

4. Core level states of Ba and Sr

The XPS spectra of Ba 4d and Sr 3d core levels are shown in figure 5. Both spectra revealed two sets of peaks. Each set is clearly separated into two, with a 2.59 eV interval for BGG and 1.76 eV for SGG. The binding energy values of the Ba 4d electrons listed in a standard data booklet are 92.6 and 89.9 eV for 4d\(_{3/2}\) and 4d\(_{5/2}\), and those of Sr are 136.0 and 134.2 eV for 3d\(_{3/2}\) and 3d\(_{5/2}\) [20], respectively. Considering the estimated value of 2.7 eV associated with the quantum numbers of Ba 4d as well as 1.8 eV of Sr 3d, the two largely separated doublets can be assigned to these quantum numbers. The intensity ratios of 2 : 3 observed in each set of peaks for both BGG and SGG agree very well with the theoretical values expected from these quantum numbers.
The endohedral positions and elements of the clathrate framework are displayed in figure 1 according to the crystallographic rules in the space group Pm3n. Supposing that the guest atoms fully occupy both the 2a and 6d sites in BGG, the observed spectrum was simulated using two-component Gaussian–Lorentzian functions with intensity ratio of 1 : 3 corresponding to the crystallographic site numbers (two 2a-site dodecahedra and six 6d-site tetrakaidecahedra in the unit cell). This assumption is very reasonable because XRD and electron-probe microanalyses indicate that full occupation of the endohedral Ba is realized in BGG. The separations of two nearest peaks between the 2a and 6d sites are 0.95 eV on average for Ba 4d.

In order to check whether the observed separation is theoretically reasonable, we have performed first-principle band calculations on BGG using the WIEN2k package program as discussed previously [15, 16]. The calculations predict that the orbital level of the 2a-site Ba is lower by 0.95 eV than that of the 6d-site one, being in good agreement with the experimental results. The band calculations also showed that the electron density at the 2a-site should be larger by only 0.06 electrons than that at the 6d-site.

Estimated difference of 0.3–0.5 electrons is needed to explain the chemical shift observed in our experiments. Therefore, the chemical shift observed between the 2a and the 6d sites cannot be explained by the difference in electron transfer degree, but instead should be caused by the different Madelung potentials created by the two cage structures.

Inspection of the Sr 3d spectrum of SGG reveals that the intensities are very different from the case of Ba 4d in BGG. More surprisingly, the Sr atoms at the 2a sites show an opposite chemical shift to the case encountered for BGG, and the intensity ratio deviates from the ideal structural stoichiometry. This can probably be attributed to the partially off-centered locations of the 6d-site Sr atoms, which results in further splitting of the spectrum. Careful analyses have led us to a successful simulation using three components instead of two, keeping the 2a- and the 6d- component ratio of 1 : 3 and introducing a twofold 6d-site component with the 1 : 3 ratio. The former ratio arises from the type-I clathrate structure as described for BGG, and the second 1 : 3 ratio is adopted based on the previous extended x-ray absorption fine structure analysis [21]. This result for SGG is very intriguing because it should reflect the environments in which the endohedral Sr atoms reside, and warrants a detailed discussion as follows.

The Sr 4s2 4p6 configuration seems to hybridize easily with the framework cluster orbitals (4sp3) due to the same principle quantum number, and this should be compared with the situation encountered for the Ba 5s2 5p6 configuration. However, the band structure studies showed that both endohedral Ba and Sr atoms have little hybridization with the framework. Our band calculations for SGG with the Sr atoms at the on-centered position also did not show any meaningful dissimilarity to that of BGG. Therefore, this case can be ruled out, and the experimental observations can be naturally interpreted by the off-centered position of the endohedral Sr atoms inside the (Ga–Ge)24 cage, as obtained from previous neutron diffraction studies [8, 12]. We then performed first-principle band calculations applying the crystal structure with off-centered endohedral Sr atoms as determined by neutron diffraction [22] for judging such possibility. The results predicted a difference in energy of 0.83 eV between the off-center 6d-site and the on-center 2a-site for Sr 3d, therefore smaller when compared to 0.95 eV for the two on-centered site models. This indicates that the off-centered positioning can modify the hybridization between the endohedral atomic orbitals and the surrounding framework orbitals, but such modifications are not sufficiently large to explain the observed inverse positions by −0.89 eV for Sr 3d.

Although the neutron experiments suggested that the probability of the endohedral Sr atom positions inside the polyhedral cage is the highest at the 24k-sites being a little bit away from the 6d-sites [22], the band calculations employing this off-centered model were not able to explain the observed large change as discussed earlier. It should be mentioned that two important factors were not accounted in the present band calculations. One refers to possible electron correlations. Fortunately, the type I clathrates are not categorized into such strong electron-correlated systems. The other factor involves...
dynamic motions among the equivalent atomic positions under the potentials created by the outer frameworks. Actually such time and space dependent dynamic motions showing anharmonic oscillations are not considered in the present band calculations. Two modes have been considered so far for such rattling phonons, i.e. thermal and tunneling modes. Recent Raman scattering results \[11\] combined with first-principle calculations \[23\] displayed splitting of the 6d atomic position of the endohedral Sr atoms under quartic potentials. Because of the 0.04 meV splitting in phonon modes between the ground state and the first excited state, as well as the negligibly small temperature dependences of the two \(T_{2g}\) Raman modes, the dominant thermal rattling is suggested.

However, when we carefully checked the Sr 3d core spectra between 20 K and 300 K, they showed negligible temperature dependences although their linewidth increased slightly at higher temperatures. Meanwhile, similar atomic Debye–Waller displacement parameters, increasing with temperature, are reported among BGG, SGG and EGG. Therefore, the observed anomalous feature is not due to the thermal rattling. The tunneling has also been discussed as another mode to compete the thermal one. Keeping in mind that the energy difference between the two 6d Sr peak positions in the core level spectra is about 0.73 eV, which is four orders of magnitude larger than the rattling energy, the anomalous feature in the XPS core level cannot be caused by the tunneling. Taking into account all the arguments described here, the remaining most plausible explanation is that the outer Ga–Ge cages are differently reconstructed depending on the type of endohedral atoms. This reconstructed cage structure creates the different Madelung potentials necessary to confine the endohedral Sr atoms and exert a large influence on their energetics.

Our interpretation can further be supported by analyzing the core spectra measured for \(\text{Sr}_8\text{Ga}_{16}\text{Si}_{30}\) (SGS) and EGG. Figure 6 shows the Sr 3d spectra in SGS. It is now obvious that each set of peaks corresponding to the quantum numbers \(3/2\) and \(5/2\) consists of three components. The right-side peak of Sr 3d\(3/2\) and the left-side peak of 3d\(5/2\) overlap. Assuming the same constraints used for the simulations of SGG, we successfully reproduced the experimental data. This strongly supports that our interpretations for SGG is correct.

The Eu 4d core level spectrum in EGG is complex. The multiplet observed at low energies is the well known \(9D\) splitting starting with \(J = 2\) to 6 (quintet) \[24\]. The featureless peak observed at higher energies is due to the 4f–4f electrostatic and the spin–orbit interactions. However, the spectrum intensity ratio of \(9D\) was different from the ideal one. Supposing that Eu resides at the 2a and 6d sites with the 1 : 3 ratio and that both show quintet structure, the whole spectrum shape could be reasonably simulated. The 6d component shows lower chemical shift than the 2a one, which is similar to the case of Sr 3d in SGG. It is very important that the spectrum can be fitted using one type of 6d, but not 6d(1) and 6d(2), together with 2a, and this is different from what was observed in SGG. If we consider that the 6d Eu atoms locate under four off-centered potential minima, as unambiguously displayed by neutron diffraction \[8\], this indicates that Eu shows time- and space-dependent rattling motions. Earlier Mössbauer studies showed the evidence of tunneling from the viewpoint of the missing hyperfine structure as well as the nearly temperature independence of the 6d Eu structure \[10\], in agreement with our studies.

5. Framework structure

The possibility of different Ga–Ge cage structures, modified by the requirements of endohedral atoms, naturally led us to investigate the core level spectra of the cage components themselves. The Ga 3d core level spectra are quite different among BGG, SGG and EGG even without any simulation, as shown in figure 7. There are three atomic sites in the cages, that is, 6c, 16i and 24k, and the 6c positions are only included in the larger 24-cage as shown in figure 1. In principle, the spectra could be deconvoluted using these three components corresponding to the crystallographic sites with the quantum number splitting of Ga 3d\(3/2\) and \(5/2\). However, due to a smaller resolution, a single
Figure 7. Core-level spectra of Ga 3d measured at 20 K.

refinement could hardly be achieved. Therefore, first two peaks, corresponding to the quantum numbers, were fitted with a separation of 0.45 eV [25], and then each peak was deconvoluted using three components according to the crystallographic sites. We considered the main separation of the two spectral components with an intensity ratio of 2 : 3, shown by red (3d 3/2) and blue (3d 5/2) peaks, in terms of the Ga 3d spin–orbit coupling for BGG, SGG and EGG. Using least-squares method, each separated component was deconvoluted as three peaks using the Gaussian–Lorentzian function with a different Gaussian/Lorentzian component ratio. The component ratios were 34%, 28% and 38% for BGG, 12%, 51% and 37% for SGG and 47%, 16% and 37% for EGG.

Our experimental results suggest that the compositional distribution in the larger cages is not uniform in SGG, and two types of different compositional cages should exist: one corresponding to the on-centered mode and the other to the off-centered mode as shown in figure 2. Further attempts have been made to determine the atomic positions of Ga and Ge by the conventional XRD using high-quality single crystals in our laboratory. However, useful information could not be obtained due to the very similar scattering factors between Ga and Ge atoms. In such a case, anomalous x-ray scattering is of prior importance for these compounds. In addition, it should be noted that the core level shifts in Ba 4d and Sr 3d can be used as a fingerprint for determining the cage structure. Therefore, we hope that more sophisticated approaches, such as anomalous XRD and improved theoretical calculations, will be performed in the future.

6. Conclusion

The electronic states of the endohedral Ba and Sr atoms in BGG and SGG were comparatively studied. XPS experiments and theoretical calculations indicated that the valence band is mainly constructed by the Ge/Ga 4s and 4p wave functions with little contribution of the Ba/Sr valence orbitals. The 6d-site Ba atoms show the higher 4d chemical shifts than that of the 2a-site ones due to the different Madelung potentials created by the two kinds of cage structures. However, a different situation was observed in the chemical shift of the endohedral Sr in SGG. We suggest that a cage network with different Ga–Ge distribution can be made depending on the type of endohedral atoms. This may be caused by the interactions between the outer cages and the endohedral atoms, and the various potentials created by the cage distributions are automatically generated during the synthesis. Therefore, the energy potentials confining the endohedral atoms are static in origin, and the endohedral atoms will show their anharmonic oscillations under such local confining potentials in SGG. This interpretation can be further supported by analyzing Ba 4p in BGG and Sr 3p in SGG, Sr 3d in SGS and Eu 4d in EGG as well as the Ga 3d core level in these clathrates. Advanced calculations based on our model should improve the understanding of the rattling phonons.

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