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Energetics of endohedral atoms in type-I clathrates observed by soft x-ray spectroscopy

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We present an extensive soft x-ray photoelectron spectroscopy study on the core levels of the endohedral atoms of $Ba_8Ga_{16}Ge_{30}$ (BGG), $Sr_8Ga_{16}Ge_{30}$ (SGG), $Eu_8Ga_{16}Ge_{30}$ (EGG), and $Sr_8Ga_{16}Si_{30}$ (SGS) single crystals, performed at a high-energy facility. Unexpected features evidencing the different shift for the 2*a* and 6*d* sites between Ba 4*d* and Sr 3*d* are observed for BGG and SGG. The detailed analyses including theoretical support by first-principles band-structure calculations lead to the surprising conclusion that the component distributions of the larger tetrakaidecahedral cage are different depending on the endohedral atoms, which is in contrast to the past consensus that BGG and SGG have the same framework structure. The differences are further supported by analysis of the Ga 3*d* core levels. This may suggest thorough reconsiderations on earlier interpretations of experimental data.

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I. INTRODUCTION

The concept of phonon glass, electron crystal (PGEC) introduced by Slack in 1995[1] has been used as one of the most useful design methods for thermoelectric power generation materials. In the PGEC concept, heat transfer is anticipated to be suppressed by phonon scattering, even though electric transport remains high in the Bloch lattice. A realization of this concept has recently been demonstrated for type I clathrates, $M_8Ga_{16}Ge_{30}$ (M=Ba: BGG, M=Sr: SGG and M=Eu: EGG)[2,3] and applications are already under consideration due to their observed high-energy conversion efficiency.[4]

Especially for allowing real scientific insight into the PGEC concept, the energetics of the endohedral atoms confined under the potentials created by the surrounding atoms or crystal field is important. Rattling phonons with anharmonic oscillations have been the key issue, ever since elastic neutron-diffraction studies in $M_8Ga_{16}Ge_{30}$ demonstrated that the smaller Sr atom shows a wider distribution of its density map than that of the larger Ba, while the Eu atom shows an even wider quartic density distribution.[3] 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 of the hyperfine structure.[5] Raman spectroscopy has also shown unusual temperature dependencies of the vibration modes in this clathrate family[6] and a dominant thermal-mode rattling is suggested above 2 K. Although many experiments such as heat capacity, thermal transport, x-ray diffraction, and temperature-dependent inelastic neutron scattering[3,7–9] have been applied to elucidate the real nature of the rattling phonons, discussions on the microscopic origin of the anomalously low thermal conductivity are ongoing.

Here, we report anomalous features found in core-level x-ray photoelectron spectroscopy (XPS) spectra of the endohedral Ba, Sr, and Eu, which cannot be explained by the models described in many past interpretations. Unexpectedly, distinct differences have been observed when Ba 4*d* in BGG and Sr 3*d* in SGG are compared. These results strongly suggest that the outer cage structure changes depending on the type of endohedral atom present. We propose that these important factors not having been duly recognized so far should be taken into consideration to achieve a complete understanding of the rattling phonons in this system.

II. EXPERIMENT

BGG (*n* type) and SGG (*n* type) single crystals, with type-I clathrate structure shown in Fig. 1 were synthesized using a self-flux method detailed elsewhere.[8,10] Similar methods were applied to obtain *n*-type EGG and $Sr_8Ga_{16}Si_{30}$ (SGS) crystals used here for comparison. The crystal structures were refined by Rietveld analyses for the high-resolution x-ray diffraction data measured at the beam line BL02B2 of the high-energy beam line factory of SPring-8, using the RIETAN 2000 analytical package program.[11] Soft XPS measurements were performed under vacuum of

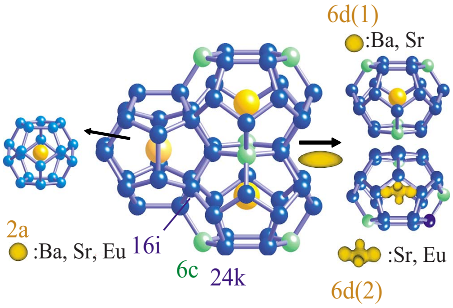

FIG. 1. (Color online) A part of the structure of type I clathrates. Two sites accommodate the endohedral atoms, denoted by $2a$ and $6d$, and the larger $6d$ site affords more freedom of motion. Two schematic models for the distribution of endohedral atoms at the $6d$-site are also shown.

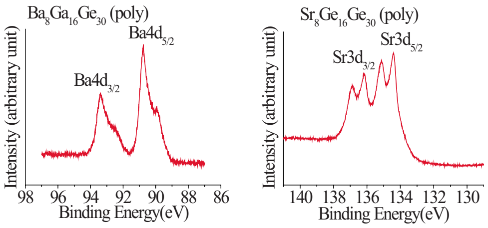

FIG. 2. (Color online) Core-level spectra of Ba $4d$ and Sr $3d$ for BGG and SGG polycrystals measured at 20 K.

10^{-8} Pa at the BL25SU beam port of SPring-8 as reported elsewhere.[12,13] Clean sample surfaces were prepared by cleaving the ingot samples directly in a chamber. The sample surfaces were irradiated with a 776 eV soft x-ray beam with a 10 meV bandwidth and the density of states at 20 K was recorded by measuring the kinetic energy of the ejected electrons using a Scienta high-resolution energy analyzer. The core levels of Ga $3d$, Ba $4d$, Sr $3d$, and Eu $4d$ were measured. In order to determine whether the spectra are intrinsic and not influenced by surface contributions, more than 10 different batches of samples were measured, and all of the spectra showed the same line shape.

Other trivial contributions to the core-level spectra, such as surface contaminations, segregations and inclusions in the samples, were excluded because the core-level spectra were not affected by changing samples, cleavage trials, and the positions irradiated on the samples. The reproducibility of the measured spectra was high because the experimental procedures were carefully repeated each time. The most recent information of penetration depth in 776 eV can be available from SPring-8.[14] Measurements on Yb were made as a function of excitation photon energy from 16.8 to 1500 eV. The data show that the contribution from the surface to the photoelectron spectra due to the surface core-level shifts is subdominant (less than 10%) when the kinetic energy of photoelectrons emitted from the target core level exceeds 400–700 eV. Since the Ge and Ga are much lighter elements than Yb and atomic densities of these clathrates are lower than that of Yb, the inelastic mean-free paths in BGG and SGG are expected to be larger than that of Yb. Therefore, according to the above mentioned facts, the surface contributions to those of the bulk are concluded to be less than 10% and would not seriously affect the analysis of the present paper. The purpose of single crystals in the present experiments is to improve XPS spectral resolution. The XPS spectra of polycrystalline BGG and SGG are displayed in Fig. 2 and it is clear that if the spectra are compared to those of single crystals shown later, the spectra of single crystals have a higher resolution without any change in spectrum shape.

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 exchange-correlation energy parameterized by Perdew-Burke-Ernzerhof was used. The cutoff energy of the plane waves was 13.2 Ry. The maximum magnitude of the reciprocal-lattice vector $G \cdot a/2\pi$ with lattice parameter a was 14, which was used in the Fourier expansion of the charge density. In the self-consistent field calculations, the Brillouin sampling was $20k$ points in the irreducible wedge. The sampling of $84k$ points was used for the density of state (DOS) calculations. In the calculations, we used the virtual-crystal approximation (VCA) to take account of Ga substitution for host Ge atoms, i.e., artificial atoms with a fractional atomic number Z are introduced. The VCA is usually used in these systems.[15] Employed atomic numbers are as follows: 31.6 at the $6c$ and the $24k$ sites and 31.75 at $16i$, where the average atomic number is 31.652 corresponding to a Ga/Ge ratio of 16/30. The guest atoms were put in high-symmetry positions for both kinds of sites.

III. RESULTS AND DISCUSSION

The XPS spectra of Ba $4d$ and Sr $3d$ core levels measured at 20 K are shown in Fig. 3. Both spectra revealed two sets of peaks. Each set is clearly separated into two peaks, with

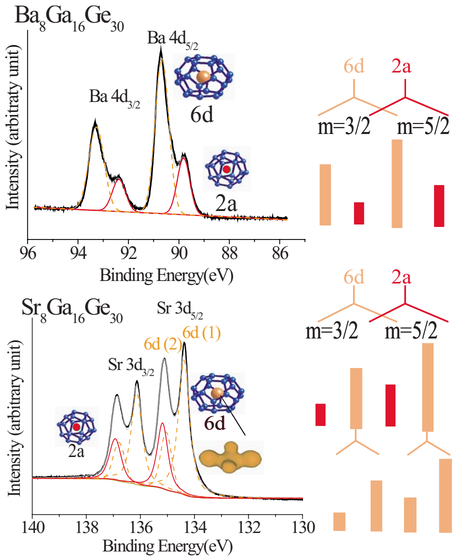

FIG. 3. (Color online) Core-level spectra of Ba $4d$ and Sr $3d$ measured at 20 K. The deconvoluted components displayed were obtained by least-squares fitting, assuming two types of Ba atoms at the cage centers in BGG. In contrast, three component simulations using one $2a$ and two $6d$ sites [denoted by $6d$ (1) and $6d$ (2)] are necessary in SGG as simply described using bar graphs.

an interval of 2.59 eV for BGG and 1.76 eV for SGG. The binding-energy values of the Ba 4*d* 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 $3d_{5/2}$, respectively.[16] Considering the estimated splitting value of 2.7 eV associated with the quantum numbers of Ba 4*d* and 1.8 eV of Sr 3*d*, the two sets of double peaks were assigned to these quantum numbers. The intensity ratio of 2:3 observed for each set of peaks of both BGG and SGG actually agrees with the theoretical values expected from these quantum numbers. Similar measurements of Ba 4*d* and Sr 3*d* core levels with different photon energies show almost the same spectra, clearly indicating that there are little surface contributions.

Supposing that the guest atoms fully occupy both the 2*a* and the 6*d* sites in BGG, the observed spectrum was simulated using two-component Gaussian-Lorentzian sum functions,[17] where an the intensity ratio of 1:3 corresponding to the crystallographic site multiplicities (two 2*a*-site dodecahedra and six 6*d*-site tetrakaidecahedra in the unit cell) was used (bar graph in Fig. 3). The separation of two nearest peaks between the 2*a* and the 6*d* sites is 0.89 eV on average for Ba 4*d*. To determine whether the observed separation is theoretically reasonable, we have performed first-principles band-structure calculations on BGG using the WIEN 2 K package program.[18]

The calculations indicate that the orbital level of the 2*a*-site Ba is 0.95 eV lower than that of the 6*d* site one, thus being in good agreement with the experimental results. The band-structure calculations also showed that the electron density at the 2*a* site should be only 0.06 electron larger than that at the 6*d* site. In order to explain the chemical shift observed in the present experiments, a difference of 0.3–0.5 electron is needed by rough estimations. Therefore, the chemical shift observed between the 2*a* and the 6*d* 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. To confirm the off-center effect to core-level shifts of guest atoms we have also performed the electronic structure calculations with displacement of Sr atoms from the 6*d* positions in SGG. The calculated results are similar to that of the on-center case. The ordering of the 3*d* core-level energies for Sr atoms in the 2*a* and the 6*c* positions did not change.

When we inspect the Sr 3*d* spectrum of SGG, it is immediately noticed that the spectrum intensity ratio is very different from the case of Ba 4*d* in BGG. More surprisingly, the Sr atoms on the 2*a* sites show an opposite chemical shift to the case encountered for BGG, and the spectrum ratio deviates from the structural ideal stoichiometry. This can be attributed to the partially off-centered locations of the 6*d*-site Sr atoms, which results in further splitting of the spectrum, as discussed in the following paragraphs.

SGG spectra in Fig. 3 are carefully fitted. Both the higher and the lower sets consisting of two-component peaks apparently result from the spin-orbit coupling ($d_{3/2}$ and $d_{5/2}$) with an intensity ratio of 2:3 both in SGG and BGG. Therefore, we constrained this intensity ratio. Furthermore, considering the crystal structure of polyhedral network, the ratio of 2*a* to 6*d* sites of 1:3 was also used as another constraint and these are common constraints for simulation of both BGG and SGG. With the above constraints, two types of simulations were carried out for SGG. Using two components for each set of spectra with the same quantum number and leaving the freedom of linewidth, we have succeeded to simulate the spectra. However, the linewidth of the 6*d*-site peak became unreasonably broad. Another simulation was made assuming three components: one for 2*a* and the other two for 6*d*. In this case, we added another constraint besides the general constraints described earlier, i.e., the intensity ratio between the two 6*d* peaks is 1:3, according to the extended x-ray absorption fine-structure (EXAFS) experimental data and their interpretations.[19] We have successfully simulated the spectra. The latter simulation using three components was statistically better than the former two-component one. We have searched for other possibilities in order to improve the fit, and the one shown in Fig. 3 was found to be the best. These careful analyses, using three components instead of two, have led us to a successful simulation as displayed in Fig. 3 with the bar graph. This result for SGG is intriguing because it should reflect the environments in which the endohedral Sr atoms reside, and warrants a detailed discussion as follows.

Our band-structure calculations for SGG with the Sr atoms at the on-centered position did not show any meaningful dissimilarity to that of BGG. Therefore, a natural idea for interpreting the experimental observations is the off-centered position of the endohedral Sr atoms inside the $(\mathrm{Ga-Ge})_{24}$ cage, as suggested by previous neutron-diffraction studies.[3,9] We then performed first-principles band-structure calculations applying the crystal structure with off-centered endohedral Sr atoms as determined by neutron diffraction.[20] The results predicted a difference in energy of 0.83 eV between the off-center 6*d* site and the on-center 2*a* site for Sr 3*d*, which is smaller than 0.95 eV for the two on-centered site model. This indicates that the off-centered positioning can modify the hybridization between the endohedral atomic orbitals and the surrounding framework ones, but such modifications are far from being able to explain the observed inverted positions shifted by-0.89 eV for Sr 3*d*.

Two important factors were not taken into account in the present band-structure calculations. One refers to possible electron correlations, but fortunately the type I clathrates are not categorized as such strong electron-correlated systems. The other factor is dynamic motions among the equivalent atomic positions under the potentials created by the outer framework atoms. Two modes have been considered so far for such rattling phonons, i.e., thermal and tunneling modes. From recent Raman spectroscopy[6] and neutron elastic-scattering studies,[3] small temperature dependencies have been reported. Therefore, the observed anomalous feature is not due to the thermal rattling, because almost negligible temperature dependencies were observed in the present XPS spectra for BGG and SGG. Tunneling has also been discussed as another mode to compete with the thermal one. Keeping in mind that the energy difference between the two 6*d* Sr peak positions in the core-level spectra is about 0.73 eV and therefore four orders of magnitude larger than the reported rattling and tunneling in the 0.02–4.4 meV range (in particular in SGG the energy is 4.4 meV,[21] and in contrast,

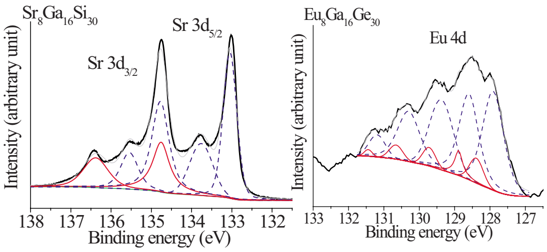

FIG. 4. (Color online) Core-level spectra of Sr 3*d* and Eu 4*d* measured at 20 K. Three component simulations using one 2*a* and two 6*d* sites can well describe the features for SGS, while one 2*a* and one 6*d* sites can simulate all the features of EGG.

the tunneling energy is much smaller at about 0.02 meV,[5,22]), the anomalous feature in the XPS core level *cannot* be caused by tunneling. Taking into account all the arguments described here, the remaining most plausible explanation is that the outer Ga-Ge cages are reconstructed differently depending on the type of endohedral atoms. The reconstructed cage structure creates different Madelung potentials necessary to confine the endohedral Sr atoms and exerts a large influence on their energetics.

Our interpretation is further supported by analyzing the core spectra measured for $Sr_8Ga_{16}Si_{30}$ (SGS) and EGG. Figure 4 shows the Sr 3*d* spectra in SGS. It is obvious that each set of peaks corresponding to the quantum numbers (3/2 and 5/2) consists of three components in the case of SGS (the right-side peak of Sr $3d_{3/2}$ and the left-side one of $3d_{5/2}$ overlap). For simulating the spectra for SGS in Fig. 4, the same common constraints were used leaving freedom in linewidth. The clear resolution of the three components for each quantum number ensures the quick convergence and the quality of the fit, indicating that our approach to simulate the SGG spectra is reasonable.

The Eu 4*d* core-level spectrum in EGG seems complex at first glance, but the multiplet observed is the well-known ^{9}D splitting starting with $J=2$ to 6 (quintet).[23] Supposing that Eu resides at the 2*a* and 6*d* sites in a 1:3 ratio and both sets of peaks show quintet, the whole spectrum shape could be reasonably simulated. In addition, we made another constraint using the same linewidth corresponding to the 2*a* and 6*d* components among the quintet, respectively, and we were able to obtain a unique solution. The 6*d* component shows a smaller chemical shift than the 2*a* one, which is similar to the case of Sr 3*d* in SGG. It is very important that the spectrum could be fitted using one type of 6*d* together with 2*a*, which is different from the case of SGG. If we take into consideration the fact that the 6*d* Eu atoms are located in four off-centered potential minima unambiguously evidenced by neutron diffraction,[3] this seems to indicate that Eu shows time- and space-dependent rattling motions. From Mössbauer studies, tunneling has been suggested due to the loss of hyperfine structure of the 6*d* Eu atoms with a nearly temperature independent frequency.[5] Our XPS observations are consistent with these previous reports.

The possibility of different Ga-Ge component cage structures, being modified by dictating to the endohedral atoms, naturally led us to investigate the core-level spectra of the cage components themselves. The Ga 3*d* core-level spectra

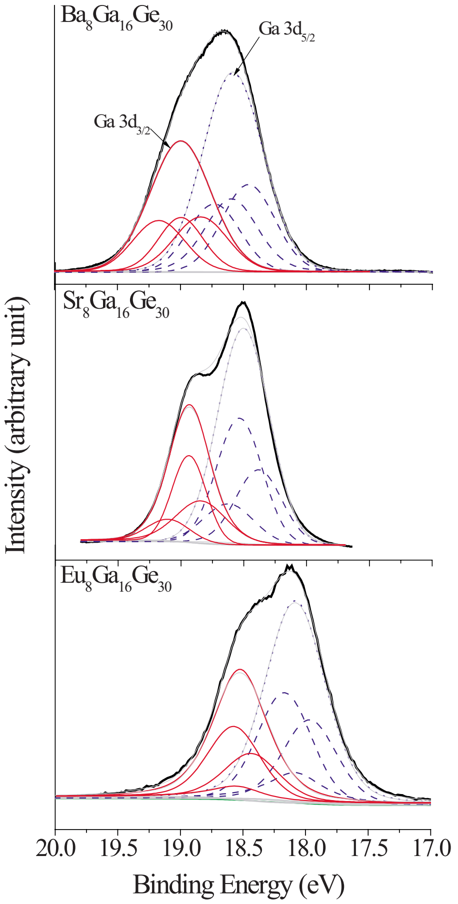

FIG. 5. (Color online) Core-level spectra of Ga 3*d* measured at 20 K.

among BGG, SGG, and EGG are quite different even without any simulation. In the case of simulation for Ga 3*d* spectra in Fig. 5, the situation was different from those in Figs. 3 and 4. There are three atomic sites in the cages, that is, 6*c*, 16*i*, and 24*k*, and the 6*c* positions are only included in the larger 24-cage as shown in Fig. 1. In principle, the spectra could be deconvoluted using these three components corresponding to the crystallographic sites with the quantum number splitting of Ga 3*d* 3/2 and 5/2. However, due to a smaller resolution, a single refinement could hardly be achieved. Therefore, first two peaks corresponding to the quantum numbers were fitted with a separation of 0.45 eV,[24] and then each peak was deconvoluted using three components according to the crystallographic sites. Considering the main separation of the two spectral components with an intensity ratio of 2:3, shown by red ($3d3/2$) and blue ($3d5/2$) peaks, in terms of the Ga 3*d* spin-orbit coupling for BGG, SGG, and EGG using least-squares method, each separated component was deconvoluted as three peaks using the Gaussian-Lorentzian sum function with a different Gaussian-Lorentzian value. The component ratios were 34%, 28%, and 38% for BGG, 12%, 51%, and 37% for SGG, and 47%, 16%, and 37% for EGG.

It was reported that anomalous x-ray scattering is useful to measure the network occupancies,[25] and that Ga atoms show an occupation preference for the 6*c* site between *p* and *n* BGG's because of the occurrence of energetically unfavorable Ga–Ga bonds. Then the third lowest energy peaks can be assigned to the 6*c* sites since only the percentage of these peaks is close to the ideal 6*c*-site Ga occupation of 37.5% (6/16) estimated from the structure, and thus Ga atoms show a 6*c*-sites preference. The other peaks corresponding to either the 16*i* or 24*k* crystal sites were different among BGG, SGG, and EGG. Although the simulation cannot be accurate due to a smaller resolution of the peaks and may not be unique, the shape of the spectra is obviously different in appearance in each case, indicating that a polyhedral cage rearrangement takes place by dictating to the endohedral atoms. Should Ga be replaced by Ge in a different ratio, it could cause a shift in the peak position of the off-centered atoms due to modified Madelung potentials, and this would explain the present experimental data.

The same observations were obtained essentially independent of thermal histories, when we prepared samples with the same stoichiometry of each precursor. Furthermore, the same experimental results were obtained both for single crystals and polycrystalline samples. It is evident that the off-centered displacement of the endohedral atoms can be dictated by the relationship between endohedral atoms and the particular Ga-Ge distribution site. The atomic motions of the endohedral Ba and Eu atoms in the 2*a* sites are always in an on-centered mode. However, the motions at the 6*d* site change from an on-centered mode in BGG to both on-centered (25%) and off-centered (75%) modes in SGG, and shift to a completely off-centered mode in the case of EGG.[3,19] The present 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 one as shown in Fig. 1. Further attempts have been made in order to determine the atomic positions of Ga and Ge by the conventional x-ray diffraction using high quality single-crystal samples 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 experiments are believed to be of prior importance for these compounds. In addition, it should be noted that the core level shifts in Ba 4*d* and Sr 3*d* can be used as a fingerprint for determining the cage structure. Therefore, we hope that more sophisticated approaches, such as anomalous x-ray diffraction and high quality theoretical calculations, will be performed in the future.

IV. CONCLUSION

In conclusion, the electronic states of the endohedral Ba and Sr atoms in BGG and SGG were comparatively studied. The 6*d*-site Ba atoms showed higher 4*d* chemical shifts than those of the 2*a*-site ones due to the different Madelung potentials created by the two different cage structures. However, a different situation was observed in the chemical shift of the endohedral Sr in SGG. We concluded that a cage network with different Ga-Ge distribution forms depending on the type of endohedral atoms. It has been reported that the carrier tuning in SGG and BGG affects the transport properties. This tuning may be directly related to the cage reconstruction described in the present work. However, our data do not allow us to answer this question unambiguously at this stage. The energy potentials confining the endohedral atoms are static in origin and the endohedral atoms show anharmonic oscillations under such local confining potentials in SGG. Although some aspects are not fully understood yet, our results evidence the importance of the cage reconstructions and calls for a better understanding of the rattling phonons in these systems through more sophisticated theoretical calculations, which are outside the scope of the present study.

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