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Giant dipole resonance of Ba in Ba_8Si_{46}: An approach for studying high-pressure induced phase transitions of nanostructured materials

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The giant dipole resonance of Ba embedded into the complex Si host lattice structure of Ba_8Si_{46} has been observed under ambient and high-pressure conditions. The measurements have been accomplished using nonresonant inelastic x-ray scattering for different momentum transfers. The resonance appears as a broad feature between 100- and 150-eV energy loss for low momentum transfer but vanishes for high momentum transfer. Calculations within the time-dependent local-density approximation have been performed by means of a real-space multiple-scattering Green's-function approach. The results reproduce the shape and the width of the observed resonance. Modulations of the giant resonance spectra are predicted by computations ranging from ambient pressure up to 20 GPa which can be used to study the local environment of the Ba guest. A corresponding experimental setup for high-pressure studies is presented, potential applications to study the phase transitions of Ba clathrates are discussed, and first experimental results are shown.

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I. INTRODUCTION

Silicon clathrates are networks built up from different Si nanocages that can contain guest atoms. These materials have attracted much interest in the last years due to their special physical properties. Depending on the guest atom the clathrates exhibit a wide range of behavior from superconductivity to magnetic order. The guest atom can also induce special band-electronic and thermoelectric structure in the system. Finally, for various doped clathrates surprising high-pressure properties have been revealed (see, e.g., Ref. 1 for a comprehensive overview). The Si clathrate Ba_8Si_{46} is of special interest showing three phase transitions under hydrostatic pressure. Around 5–7 GPa Kume *et al.*[2] found a reversible collapse of vibrational Raman modes giving a hint to a second-order phase transition. This result is supported by x-ray-absorption near-edge structure (XANES) measurements of the Ba L_{III} edge by San Miguel *et al.*[3] indicating an energy shift of the edge onset position. The transition is attributed to a displacement of the Ba dopants[2,4] from the center of the cages which should also lead to electronic reconfiguration between the Ba and the Si atoms of the host lattice.[3] However, by extended x-ray-absorption fine-structure (EXAFS) analysis a maximum displacement of the dopants of only 0.3 Å has been estimated.[3] Between 11.5 and 14 GPa San Miguel *et al.*[3] observed a drastic reduction of the lattice constant by x-ray diffraction (XRD) whereas the diffraction pattern shows no change in the crystal structure. The mechanism of this isostructural volume collapse is not fully understood. So it is predicted by Yang *et al.*[4] by employing band-structure calculations that the Fermi surface changes dramatically in the region of the volume collapse. Iitaka,[5] instead, proposed that some of the Si atoms are released from the Si_{46} network by pressure leading to vacancies and thus to a smaller lattice constant without a change of the structure visible for XRD. Finally, above 40 GPa Ba_8Si_{46} becomes irreversely amorphous.[1] To determine the mechanism of the phase transitions a study of the changes in the local environment and the electronic structure of the guest atom is required.

Provided that the enclathrated atoms show atomic giant dipole resonances, as is the case for atomic Ba, their study can be used to obtain a deeper understanding of its local and electronic structure. The giant dipole resonance of atomic and ionized Ba in the 4*d*-*f* transition regime is an extensively studied phenomenon caused by collective excitations of 4*d* electrons.[6–9] Shape and strength of such giant resonances are at a first view an intrinsic feature of the atom itself. However, when such an atom is placed inside complex surroundings, e.g., cagelike nanostructures, modulations in the fine structure of the resonances are predicted.[10] They can be directly attributed to the symmetry of the cage and the position of the intercalated atom. This was emphasized by Luberek and Wendin[11] who presented calculations of the x-ray-absorption near-edge spectra of endohedral fullerenes Ba@C_n. The modeled spectra show fingerprintlike structures in the shape of the giant resonance depending on the size and the shape of the carbon cages as well as the position of the guest atom. Thus these features are very sensitive to changes of the local environment of the Ba atom and are caused by standing waves of the scattered electron within the carbon cages. A strong distortion of the Xe 4*d*-*f* giant resonance in Xe@C_{60} was predicted recently by computations of Amusia *et al.*[12] Experimentally, the Ba giant resonance has been observed in a solid for, e.g., $YBa_2Cu_3O_{7+x}$.[13] In 2005 experimental evidence was found in ionized Ce@C_{82} by Mitsuke *et al.*[14] which shows that such a resonance appears when the resonating atom is trapped inside a complex cagelike environment. However, the latter experiment indicates the existence of the resonance but hardly allows conclusions on its particular shape and shape modulation. Ba_8Si_{46} has a comparable structure to the Ba@C_n network and therefore the Ba giant resonance spectrum in the clathrate is expected to be likewise sensitive to its surrounding. This is of special interest in the view of high-pressure studies as changes in the local environment, e.g., off-center positions of the guest atoms in the Si cages, can be induced across phase transitions and would manifest themselves in the modulation of the resonance's shape.

With the focus on the future potential of high-pressure experiments, nonresonant inelastic x-ray scattering (NRIXS) is the only method to study giant resonances under extreme pressure. It is complementary to soft x-ray absorption and electron energy-loss spectroscopy since low-energy transitions can be measured under experimental conditions which exclude electrons and soft x rays as probes. The measured quantity in such experiments can be directly related to the dynamic structure factor $S(\mathbf{q},\hbar\omega)$ where $\mathbf{q}$ is the momentum transfer and $\hbar\omega$ is the energy loss. The incident energy can be chosen freely and thus allows the study of shallow absorption edges (between a few eV and 1 keV) using hard x rays of about 10 keV. This yields a high bulk sensitivity and makes high-pressure experiments using, e.g., diamond-anvil cells feasible.[15,16] Varying the scattering angle, i.e., the momentum transfer q, the spectra can be measured in the dipole limit (low q) or with dominating contributions from nondipole transitions (high q) (see, e.g., Refs. 17 and 18). As long as the dipole approximation is valid NRIXS spectra measured for energy losses close to a core electron binding energy can be compared with x-ray-absorption spectra measured with incident energies in the regime of the binding energy.[19] High-pressure NRIXS studies have been restricted up to now to K edges of low Z elements. Due to the very low core-level cross section for the study of heavier elements the exploration of alternative edges is necessary. It has been shown recently that the Ba $N_{\text{IV,V}}$ edges in Ba_8Si_{46} are accessible using NRIXS.[20]

In this paper a detailed study of the Ba giant dipole resonance in the complex silicon clathrate network of Ba_8Si_{46} at ambient and high pressure is presented with reference to the structural and electronic changes in the system. Spectra have been measured at different momentum transfers q using NRIXS and are compared to q-dependent calculations performed with a real-space multiple-scattering (RSMS) Green's-function approach within local-density approximation[21] (LDA), and RSMS x-ray-absorption calculations within time-dependent local-density approximation[22] (TDLDA). In the latter calculations the distortion of the Ba giant resonance's shape for different Si environments is emphasized. Moreover, a setup for high-pressure experiments on Ba_8Si_{46} is described and first results are presented along with theoretical predictions of the resonance's shape modulation at high pressure. The experiments performed under ambient and high-pressure conditions are described in Sec. II. Within Sec. III the theoretical approaches for the calculations of the measured spectra are presented and it is followed by a discussion of the results in Sec. IV. Finally, the conclusion and a short outlook are given.

II. EXPERIMENT

The ambient pressure experiment was performed at beamline ID16 of the European Synchrotron Radiation Facility (ESRF) using a crystal spectrometer in Rowland-circle geometry. The analyzer energy was fixed at 12.4 keV at the Ge(880) reflection of the spherical Ge analyzer crystal. The spectra were measured by scanning the incident energy using a Si(111) monochromator with a simultaneous adjustment of the undulator gaps. The spot size of the x-ray beam at the sample position was $50\times100\ \mu m^2$ (horizontally × vertically). An energy resolution of 1.6 eV was achieved. The Ba_8Si_{46} sample, a fine polycrystalline powder, has been prepared as described in a previous paper[20] and precharacterized by x-ray diffraction. The powder was pressed into an aluminum sample holder and measured in reflection geometry for momentum transfers of 1.50 and 6.42 a.u. The high-pressure measurements were accomplished at the Taiwan beamline BL12XU of SPring-8. A spherical Si(777) analyzer was used with a fixed analyzer energy of 13.85 keV. A total-energy resolution of 2 eV dominated by the incident beam was obtained. The incident radiation was focused to a spot size of $20\times25\ \mu m^2$ at the sample position. The high pressure was applied by means of a Merrill-Basset diamond-anvil cell (DAC). The Ba_8Si_{46} powder was loaded into a drilled hole of 125-μm diameter in a preintended 100-μm-thick Be gasket together with a ruby chip as pressure calibrant for standard luminescence method. This gasket was placed between the cut end face of the diamonds within the DAC. The beam path was chosen through the Be gasket and a tungsten slit of $50\times500\ \mu m^2$ mounted in front of the analyzer arm was brought close to the gasket to reduce scattering from Be. Pressures of 1 and 8 GPa were applied and the Ba giant resonance was measured in transmission geometry at a scattering angle of 20° (q=1.29 a.u). All measured spectra were normalized with a monitor signal and corrected for the background, absorption, and scattering cross section.[20]

III. THEORY

The silicon clathrate type I has the space group $Pm\bar{3}n$ and it consists of two different types of Si cages, Si_{20} and Si_{24}, where each Si atom is shared by four cages. The unit cell consists of 46 Si atoms forming two dodecahedra and six tetrakaidecahedra, so that the number of the larger cages is three times the number of the smaller ones. With the Ba atoms occupying the eight resulting cages this leads to the structure formula Ba_8Si_{46}. According to Fig. 2 of Ref. 3 the lattice constant at ambient pressure of about 10.35 Å decreases to 10.3, 10.1, and 9.6 Å for 1, 8, and 20 GPa, respectively.

The momentum transfer dependence of the NRIXS spectra was calculated with an adaptation of the real-space multiple-scattering (RSMS) approach FEFF8.2 (Ref. 23) for NRIXS.[21] The contributions from Ba inside a small and a large cage were calculated separately and the resulting spectra were the sum weighted by the multiplicity of the cages as discussed above. The spectra of the Si *L* edges were calculated for the three different symmetry positions occurring in the Si_{46} network and weighted accordingly. Finally, all calculated spectra were convoluted with the experimental resolution of 1.6 eV. The measurements were performed at a finite momentum transfer so that also nondipole transitions appear. Therefore the contribution of Ba 4*d*-*d* monopole transitions to the total Ba_8Si_{46} spectum was extracted from the computations which appears for energy losses at about 98 eV. Contributions from other nondipole transitions were found to be negligible within the computation. The near-edge regime of all spectra was calculated by inversion of the full-multiple-scattering matrix for a cluster of about 200 atoms. For the far-edge region the path expansion was used with a maximum path length of 12 Å.[24] Although this theoretical approach is able to calculate the momentum transfer dependence of NRIXS spectra it cannot account for collective phenomena which play an important role in giant resonances.

Collective phenomena can be incorporated in the dipole limit employing the TDLDA implementation of the FEFF code.[22] The average over the different contributions to the spectra were calculated the same way as was done for the *q*-dependent case. The total x-ray-absorption spectrum (XAS) is modeled by a sum of all Ba and Si contributions and can, within the dipole limit, be compared to the measured NRIXS spectrum. TDLDA calculations were performed within the random-phase approximation (RPA) and with the exchange correlation kernel f_{xc} by Ankudinov, Nesvizhsky, and Rehr[22] (ANR). In RPA only the external electromagnetic field of the x rays is screened by core polarization whereas ANR also includes the frequency-dependent screening of the interaction between the excited electron and the core hole. The calculations for the Ba_8Si_{46} under high pressure have been performed in the same way as for ambient pressure. The structure was assumed to be unchanged apart from the lattice constant which was chosen according to Ref. 3 as described above.

IV. DISCUSSION

The NRIXS spectra of Ba_8Si_{46} for the low and the high momentum transfer measured at ambient pressure are shown in Fig. 1. The Ba $N_{IV,V}$ edges (92.6/89.9 eV) are indicated by A, the onset of the underlying Si $L_{II,III}$ (99.8 eV) and Si L_I edges (150 eV) of the host lattice by C and D, respectively. The intense broad feature denoted by B appears only for the measurement in the dipole limit with low momentum transfer and is absent for large *q*. At such high momentum transfers single-particle hole instead of collective excitations are probed and the weight of contributions from multipole transitions is increased. Therefore feature B can be attributed to the 4*d*-*f* giant dipole resonance of Ba. It shows good agreement in energy position and width with the experimental photoabsorption cross section of atomic Ba as discussed by Richter *et al.*[7] These results are compared with computations of the *q*-dependent NRIXS spectra in Fig. 1. The *q* dependence of the underlying Si edges is reproduced very well by the calculations. Since this approach does not use the time-dependent density-functional theory (TDDFT) the observed resonance B originating from collective 4*d* electron excitations[25] cannot be reproduced in the dipole contribution. The spectral weight of the dipole transitions predicted by the computations is transferred to the broad resoncance peak at higher energy losses in the experiment. Also, for high momentum transfer the calculations are not able to model the Ba $N_{IV,V}$ edge onset A adequately. These results emphasize that collective effects have to be accounted for.

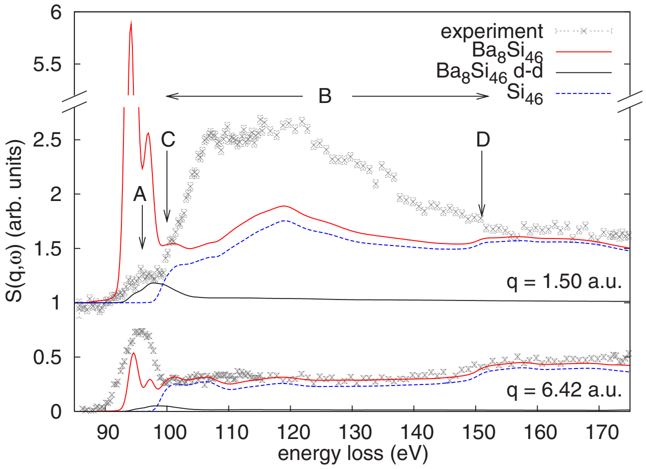

FIG. 1. (Color online) Experimental NRIXS spectra of Ba_8Si_{46} for $q=1.50$ a.u. (top) and $q=6.42$ a.u. (bottom) with associated RSMS calculations for the Si contribution and the full Ba_8Si_{46} spectrum. The contribution arising from Ba 4*d*-*d* excitations is indicated separately. A is the Ba $N_{IV,V}$ edge, C and D are the onsets of the underlying Si $L_{II,III}$ and L_I edges. The broad feature B only visible in the dipole limit can be attributed to the Ba 4*d*-*f* giant dipole resonance.

The TDLDA computations are compared with the experimental spectra of the giant resonance for low momentum transfer in Fig. 2. The overall agreement between experiment and calculations is very good. The width and the relative strength of the giant resonance with respect to the calculated Si edges agree very well with the experiment. The comparison of both calculations show that the general feature of the giant resonance can already be explained within RPA. Nevertheless, the inclusion of photoelectron-core-hole screening improves the agreement at the onset of the resonance. Remaining differences between the experiment and the theory above 115 eV might be related to the onset of double ionization as discussed by Richter *et al.*[7] Moreover, for finite *q*, as is the case for the experimental data in this work, still a certain nondipolar contribution is expected which is not accounted for in the calculated XAS spectra. The inset of Fig. 2 presents the calculations of the Ba contribution from the two different cages. They show a significant modulation of the giant resonance which is comparable to effects discussed by Luberek *et al.*[11] for Ba@C_n. These spectra indicate that the shape of the Ba 4*d*-*f* giant resonance in Ba clathrates or similar structures are strongly influenced by the local environment and thus the giant resonance yields a fingerprint of the surrounding atomic configuration.

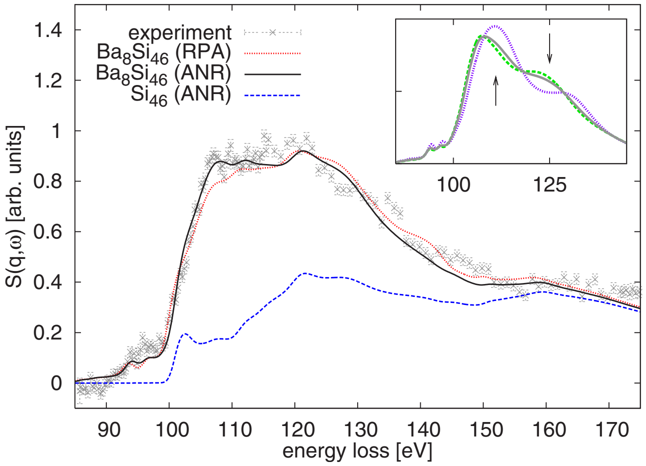

FIG. 2. (Color online) NRIXS spectrum of Ba_8Si_{46} for $q=1.50$ a.u. and calculated XAS spectra using TDLDA. The spectra have been calculated for Ba_8Si_{46} in RPA and with dynamical photoelectron-core-hole screening (ANR) as described in Ref. 22. The exclusive contribution from the Si_{46} is presented separately. The inset presents calculations for Ba_8Si_{46} (ANR f_{xc}) with the Ba absorber atom in the Si_{20} (dotted) and in the Si_{24} (dashed) cage, as the combination of the spectra weighted with the occurrence of the cages in Ba_8Si_{46} (solid).

The 4*d*-*f* giant dipole resonance of Ba enclathrated in Si cages of Ba_8Si_{46} dominates the NRIXS spectra for low momentum transfer for energy losses above the $N_{\mathrm{IV,V}}$ threshold and can be reproduced accurately by TDLDA calculations. Moreover, these computations predict significant modifications of the shape of this resonance for different local environments which indicates the potential to study phase transitions in high-pressure experiments using NRIXS spectra of giant resonances.

The high-pressure experiment was accomplished by measuring the Ba giant resonance of Ba_8Si_{46} at $q=1.29$ a.u. for pressures of 1 and 8 GPa. The results presented in Fig. 3 show the first NRIXS measurements of non-*K* edges under high-pressure conditions. The comparison between these spectra at 1 and 8 GPa with the results for ambient pressure emphasizes that the signal from the Ba_8Si_{46} can be extracted properly when measured in a DAC. These spectra are confronted with calculations of the giant resonance at pressures of 1, 8, and 20 GPa. Within the actual accuracy of the experiment it is difficult to judge if an increase of spectral weight for 4*d*-*d* excitations around energy losses of 98 eV at high pressure can be observed. Such a change could be due to an increase of filled and empty *d* bands near the Fermi level across the phase transition at 7 GPa which was discussed in Refs. 3 and 4. A conclusion on the pressure induced changes of the giant resonance's shape as predicted by theory for energy losses above 107 eV cannot be drawn within the limits of the experiment. Nevertheless, the statistics and the signal-to-noise ratio of the high-pressure signal can be improved significantly by using special DAC optimized for the use with a multianalyzer setup together with different gasket material so that detailed differences between the spectra become observable. Such experiments allow the study of giant resonances under high-pressure conditions which opens a wide field of applications concerning the structural and electronic pressure dependence of a broad range of materials.

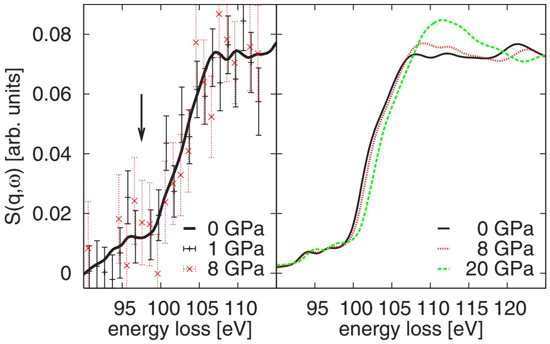

FIG. 3. (Color online) Left: Comparison of the measured Ba giant resonance onset in Ba_8Si_{46} at $q=1.29$ a.u. for ambient pressure, 1 and 8 GPa. Right: Calculated XAS spectra using TDLDA (ANR) at ambient pressure, 8 and 20 GPa. All spectra are normalized to the area between 90 and 115 eV. The arrow indicates the energy-loss regime of 4*d*-*d* monopole excitations as predicted within LDA computations employing FEFF8.2.

V. CONCLUSIONS

In conclusion, the 4*d*-*f* giant resonance of Ba was studied for Ba_8Si_{46} and, as a collective phenomenon, it was successfully modeled by calculations within TDLDA. The influence of the local environment of the Ba atom on the shape of the giant resonance both for different symmetry positions and different pressures was emphasized. Moreover, the onset of the giant resonance in the vicinity of the Ba $N_{\mathrm{IV,V}}$ edges was measured under high-pressure conditions. This gives rise to different applications for high-pressure NRIXS studies on medium- and high-*Z* elements. Measurements of the Ba giant resonance as a function of pressure by NRIXS yields enormous potential for a combined probe of changes in the electronic and local structure across phase transitions. This method can be applied in general for high-pressure studies for a wide range of nanostructured materials with resonating guest atoms caged in, e.g., clathrates or fullerenes.

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