Electronic structure of alkali-metal-doped M_8Si_{46} (M=Na,K) clathrates

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We present x-ray fluorescence measurements of alkali-metal-doped clathrates K_8Si_{46} and Na_8Si_{46}. We compare Si $K\beta_{1,3}$ ($3p \rightarrow 1s$ transition) and Si $L_{2,3}$ ($3s \rightarrow 2p$ transition) x-ray emission spectra with full potential linearized augmented plane wave band structure calculations for Si_{46}, Na_8Si_{46}, and K_8Si_{46}. A rigid band model according to which almost complete charge transfer from Na to Si takes place in Na_8Si_{46} is confirmed experimentally.

Interest in silicon and germanium clathrates has been reinforced recently by the discovery of superconductivity in $M_xNa_ySi_{46}$ (M=Na,K) with T_c=3.5–4 K (Refs. 1 and 2) and Ba_8Si_{46} (T_c=8 K).[3] Electronic band structure calculations suggest that the indirect band gap in Si_{46} clathrate is about 1.9 eV, which is 0.7 eV larger than that of crystalline silicon (*c*-Si) with cubic diamondlike structure.[4] This makes silicon clathrates promising candidates for optoelectronical applications.[5] It has been shown recently that semiconductor clathrates also have thermoelectric properties[6] and can form three-dimensional arrays of nanosized clusters.[7]

Silicon clathrates are networks of Si cages and can be considered as the Si analog to fullerenes (C_{60}) with silicon substituting the carbon. The Si cages in clathrate structures share faces to satisfy the sp^3 bonding. All Si atoms in clathrates are tetrahedrally coordinated with the Si atoms occupying the centers of slightly imperfect tetrahedrons. Although pure silicon and germanium clathrates are predicted to be locally stable, experiments have been able to synthesize the metal-doped clathrate compounds only. The interaction between the metallic impurity atoms inside the clathrate and the semiconductor skeleton modifies the electronic structure of the clathrates. A charge-balanced Zintl-phase model has been suggested for these compounds with the guest (alkali metal or alkaline earth) donating its charge to the host frame. This model was confirmed by band structure calculations of Na_8Si_{46},[8] K_8Ge_{46},[9] and $Na_2Ba_6Si_{46}$.[10] Recent experiments, however, have raised the question whether the guest is close to being neutral in some cases.[11,12] In order to estimate the validity of the rigid band model, we have carried out x-ray emission measurements of crystalline Si (*c*-Si), K_8Si_{46}, and Na_8Si_{46}. The experimental results are in a good agreement with the band structure calculations and indicate that a complete charge transfer from Na or K to Si takes place in Na_8Si_{46} or K_8Si_{46}, respectively.

Samples of Si_{46} and Na_8Si_{46} were prepared by methods similar to those described previously.[13–15] Metal silicides (K and Na) precursors were synthesized by reacting stoichiometric amounts of appropriate alkali metal with Si in an evacuated and sealed stainless steel vessel at 600 °C for 3 h. The metal silicide product was then wrapped with tantalum foil and transferred to a Pyrex or quartz tube under inert atmosphere and continued to be heated in a furnace to 360 °C

under active vacuum for 1 h. The tube was then closed under vacuum and heated at 445 °C for 20 h to produce the Si clathrate. The purity of the samples was verified by x-ray powder diffraction and the occupancy of the alkali metal was determined from Rietveld analysis. No traces of starting materials or metal impurities were found.

The first principles full-potential linear-augmented plane wave method (FLAPW) (Ref. 16) was used to calculate the electronic band structure of Si_{46}, Na_8Si_{46}, and K_8Si_{46}. The calculations were performed using the Perdew-Wang[17] reparametrization of the Ceperley-Adler free electron gas exchange-correlation potential in the local density approximation (LDA) (see Ref. 18). A plane wave cutoff (k_{max}) was chosen from the condition R_{MT}/k_{max}=8.0, where R_{MT} is the atomic muffin-tin radius. The expansion of the spherical harmonics of the wave function in the interstitial region is truncated at l_{max}=10. A 384 k-point grid (in the first Brillouin zone) and the crystal symmetry $Pm3n$ were used for the band structure calculations of Si_{46} and Na_8Si_{46}. Theoretical optimized lattice constants of Si_{46} and Na_8Si_{46} of 10.19 and 10.1735Å for K_8Si_{46} were used in the calculations.

The silicon $L_{2,3}$ ($3s3d \rightarrow 2p$ transition) soft x-ray emission spectra (XES) were measured at Beamline 8.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory employing the x-ray fluorescence endstation.[19] The excitation is nonresonant since the energy of the incident photons (118 eV) is well above the silicon L absorption edge (around 101 eV). The silicon $L_{2,3}$ XES were measured with a 600 lines/mm grating, which translates to an energy resolution of 0.1 eV.

Silicon $K\beta_{1,3}$ ($3p \rightarrow 1s$ transition) fluorescence spectra were measured using a Johann-type fluorescence vacuum spectrometer with position-sensitive detector.[20] The sample was excited by Pd L x rays and a quartz ($I0\bar{1}0$) single crystal curved to 1400 mm radius was serving as crystal monochromator. The spectra were measured with an energy resolution of 0.2–0.3 eV. (The x-ray tube was operated at 30 keV and 50 mA.)

The densities of (occupied electronic) states (DOS) of Si_{46}, Na_8Si_{46}, and K_8Si_{46} obtained from FLAPW calculations are shown in Fig. 1. The main features of total and partial density of states (DOS) are very similar for all three
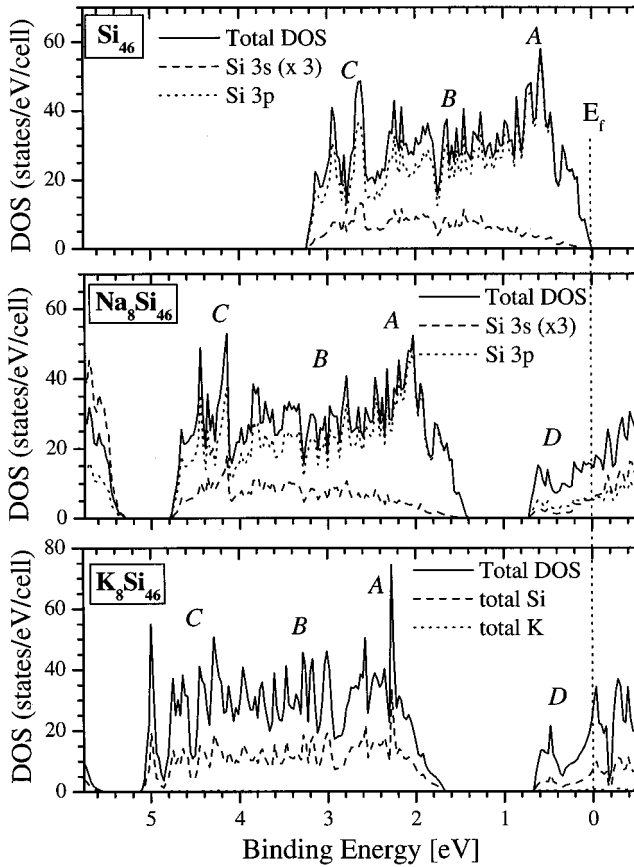
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FIG. 1. Total and partial density of states (DOS) for Si_{46} and clathrates Na_8Si_{46} and K_8Si_{46}.

FIG. 2. Si $L_{2,3}$ XES of c-Si and clathrates (dots) and Si $K\beta_{1,3}$ XES of c-Si and Na_8Si_{46}. In order to display the $K\beta_{1,3}$ spectra on the same energy scale as $L_{2,3}$, the energy of the Si $K\alpha_{1,2}$ (1740 eV, $2p_{1/2,3/2} \rightarrow 1s$ transition) has been subtracted from the original $K\beta_{1,3}$ emission energy.

compounds. Differences occur mainly in the degree of filling of the energy bands by valence electrons and the energy position with respect to the Fermi level. For Si_{46} the valence band is completely filled and the conduction band is empty giving rise to its insulating or intrinsic semiconducting behavior. In the cases of Na_8Si_{46} and K_8Si_{46} the additional sodium and potassium electrons fill the next energy band and the Fermi level is overlapping the conduction band providing the metallic properties of this doped clathrate. Similar behavior has been observed in calculated band structures of Ge_{46} and K_8Ge_{46} (Ref. 10) and Na_8Si_{46} and Ba_8Si_{46}.[21] When comparing features in different calculations, it is important to also compare the number of k-point sets since a low number can account for some structure in the DOS calculations. The conduction-band density of states does not show strong modifications upon the inclusion of metal atoms. This is due to weak hybridization between the Si_{46} conduction-band states and Na and K states and indicates that metal-metal and metal-Si interactions are ionic and that Na and K act as electron donors. Therefore alkali-metal doping introduces a narrow band labeled as D in Fig. 1. This band—directly below the Fermi level—is separated by an energy gap from the main density of electronic states (features A,B, and C) and should give rise to a spectroscopically observable feature. Its origin is in the lowest conduction band in the undoped Si_{46} clathrate. Our calculations also indicate that a significant charge transfer from Na or K to the Si skeleton is taking
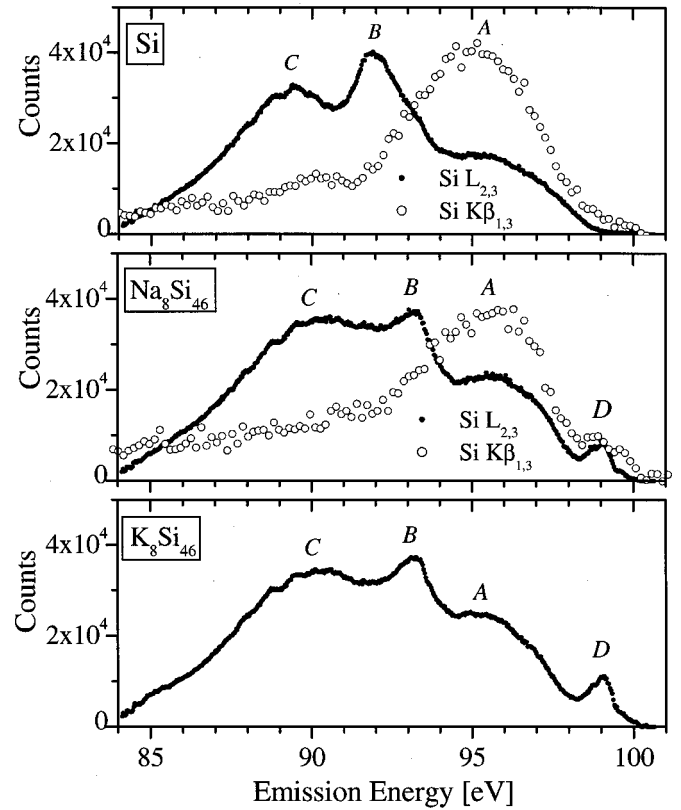
place and the rigid band model is a valid model for describing the electronic structure of these clathrates. We define the rigid band as a rigid shift of the Fermi level from the pristine Si_{46} to Na_8Si_{46} when filling empty bands with electrons from the Na atom. No rehybridization has taken place.

The spectroscopic results are in accord with recent NMR studies on Na_8Si_{46} (Ref. 22) and K_8Si_{46}.[23] These results also support large charge transfer from the alkali metal to the Si framework. This is particularly true in the case of K_8Si_{46} where the chemical shift of K is very close to that of the ion.[23] Moreover, the Knight shift of the Si atoms is larger indicating metallic character on the framework.

Si $K\beta_{1,3}$ and Si $L_{2,3}$ x-ray emission, as studied experimentally in the present work, correspond to $3p \rightarrow 1s$ and $3s3d \rightarrow 2p_{1/2,3/2}$ dipole transitions, respectively. Since a final state in the x-ray emission process in Si contains a hole in the valence band, one can expect the spectra to reflect the ground-state Si $3p$ and Si $3s$ partial densities of states following the final-state rule.[24] Figure 2 displays the Si $L_{2,3}$ emission spectra of crystalline silicon (c-Si) and Si-clathrates (Na_8Si_{46} and K_8Si_{46}) as solid dots. Three main features labeled A,B, and C are observed in both, crystalline Si and clathrates and are due to transitions from s-, d-, and sd-like bands, respectively. The feature D discussed above has its spectroscopic counterpart in the additional feature that is present at 99 eV and labeled D. Feature D is present only in

the clathrates spectra. It results from transitions of the lowest conduction band, introduced due to charge transfer from the metal atoms and corresponding to feature D in Fig. 1. The spectroscopic presence of this band demonstrates good agreement between experiment and density of state calculations and that the rigid band model is a good description.

Figure 2 also includes Si $K\beta_{1,3}$ fluorescence spectra of crystalline silicon (c-Si) and Na_8Si_{46}. Since the emission (peak A) originally occurs at 1835 eV, the emission energy has been reduced by 1740 eV (Si $K\alpha_{1,2}$: $2p_{1/2,3/2}\rightarrow 1s$ transition) in order to display $K\beta_{1,3}$ and $L_{2,3}$ spectra in the same energy window. The charge transfer peak (D) is present for Na_8Si_{46} but not as prominently resolved as in the case of the $L_{2,3}$ emission.

Recently Slack[25,26] has proposed a new criterion for finding better thermoelectric materials. According to this argument, cage compounds with a large unit cell containing encapsulated atoms that can "rattle" inside the voids will have a low conductivity. This favorable scenario does not apply if the modes effective in scattering phonons also scatter the conduction electrons and decrease the electric conductivity. Conclusively a material is desirable in which the encapsulated atoms scatter phonons but not conduction electrons and it is likely to have high electric conductivity and low thermal conductivity. Slack refers to such hypothetical material as phonon-glass and an electron-crystal (PGEC). Slack's criterion assumes that the electric conductivity is caused by the host electrons and those orbitals overlapping with the doping atoms do not affect the transport coefficients strongly. This leads us to conclude that doping atoms are not ionized and

do not couple to the conduction electrons. Our findings further indicate that Na is almost fully ionized in $(Na,K)_8Si_{46}$, which is in disagreement with the model described above. On the other hand, according to the present data and recent theoretical calculations,[27] the electronic structure of $(Na,K)_8Si_{46}$ can be described by that of Si_{46} with an inclusion of a simple rise of the Fermi level due to additional Na electrons (which is referred to in the rigid band model). This suggests that a qualitative analysis of transport properties of clathrates can be performed upon the bands of the isolated Si frame, which does not contradict with the model suggested by Slack.

To summarize we have studied the effect of doping clathrate cages with alkali metals using first-principles FLAPW band structure calculations and soft x-ray fluorescence measurements. The electronic band structure of Na_8Si_{46} and K_8Si_{46} is found to be very similar to that of the dopant-free Si_{46} except for some occupied states directly below the Fermi level that are energetically separated and give rise to an additional spectroscopic feature D. Additional electrons from Na and K atoms occupy the conduction states providing the metallic properties of Na_8Si_{46} and K_8Si_{46}.

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