Electronic structure of the $Na_{16}Rb_8Si_{136}$ and $K_{16}Rb_8Si_{136}$ clathrates

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We have calculated the electronic structure and the equations of state of the $Na_{16}Rb_8Si_{136}$ and $K_{16}Rb_8Si_{136}$ clathrates. These compounds are based on the type II silicon clathrate structure. The smaller Na (or K) atoms occupy the 20-atom cages, while the Rb atoms occupy the 28-atom cages. Equation of state, electronic band structure, and density of states calculations were performed using density functional theory in the local density approximation (LDA). The "guest" impurity atoms inside the cages modify the material electronic structure. Guest atom electrons occupy the Si_{136} conduction band states, resulting in a Fermi level shift into the conduction band of the "parent" Si_{136} framework. In qualitative agreement with the rigid-band model, the band structures display no major modifications due to the inclusion of the alkali metal guests. However, the electronic densities of states of the filled clathrates show two sharp peaks and a dip near the Fermi level. This feature may help to qualitatively explain the temperature-dependent Knight shift observed for the NMR-active nuclei in $Na_{16}Rb_8Si_{136}$. We compare our calculations with experimental results for $Na_{16}Rb_8Si_{136}$.

I. INTRODUCTION

Open framework silicon clathrates have been the subject of considerable interest in recent years. This is mainly due to structural characteristics that give rise to their unique electrical and thermal transport properties.[1] There are two structural clathrate phases: (i) Type I is a simple cubic structure in which 20-atom cages (pentagonal dodecahedra) and 24-atom cages (tetrakaidecahedra) are combined periodically in a 2 to 6 ratio. (ii) Type II has a face-centered cubic (fcc) structure in which 20 and 28-atom cages (hexakaidecahedra) are combined periodically in a 4 to 2 ratio. The cubic unit cell contains 46 atoms and 136 atoms in the type I and type II structures, respectively.[2] The clathrate framework cages can host guest atoms, which are usually alkali or alkaline earth atoms. This unique structural feature has generated considerable experimental and theoretical interest.

The main reasons for the continued interest in this compound class are (i) theoretical studies and experimental syntheses of guest filled Si and Ge clathrates showing that they have glasslike thermal conductivity,[3–6] (ii) the prediction and demonstration of electronic properties ranging from poorly semiconducting (low guest content) to semimetallic (high guest content) behavior,[7–10] and (iii) the discovery of superconductivity in $Na_xBa_ySi_{46}$ clathrates.[11] These characteristics have potential applications in semiconductor, superconductor, thermoelectric, and optoelectronic devices.

Recently, type II clathrates which simultaneously have two different types of alkali atoms in their cages have been synthesized. Bobev and Sevov have synthesized and studied the $Na_{16}Cs_8Si_{136}$ and $Na_{16}Rb_8Si_{136}$ clathrates.[12,13] These compounds are interesting because the "parent" Si framework has two different sized guest atoms in the two different sized cages. The smaller Na atoms occupy the 20-atom cages and the larger Cs or Rb atoms occupy the 28-atom cages. The interaction between the guest atoms and the Si framework modifies the material's electronic structure. In order to understand their electronic properties, a few experimental and theoretical papers have reported on some of these

materials.[14,15] A unique feature of some of these materials is the temperature-dependent Knight shift, observed in NMR experiments. This implies a complicated band structure and density of states near the Fermi level, which may cause the electronic properties to be temperature dependent.[16]

Here, we present the results of first principles calculations of the electronic properties of the $Na_{16}Rb_8Si_{136}$, $K_{16}Rb_8Si_{136}$, and guest-free Si_{136} clathrates. Our results should allow a better understanding of the electronic structure of these materials. The degree of guest atom-Si atom charge transfer can also be studied. In comparison to pristine Si_{136}, for the filled clathrates we predict an increase in the electronic density of states just below the Fermi level, and a dip at the Fermi level. This feature seems to correlate well with the temperature-dependent Knight shifts observed in $Na_{16}Rb_8Si_{136}$.[15]

II. COMPUTATIONAL DETAILS

In this study, total energies, electronic band structures, and densities of states were calculated using density functional theory (DFT), in which the self-consistent Kohn-Sham equations are solved in the local density approximation (LDA). The compounds considered ($Na_{16}Rb_8Si_{136}$ and $K_{16}Rb_8Si_{136}$) have an fcc structure and have the same symmetry as their "parent" (Si_{136}) framework lattice. Details of their crystalline structure and symmetry may be found in Refs. 17–19. The calculations were carried out with the Vienna *Ab initio* Simulation Package (VASP) using plane-wave basis sets and ultrasoft pseudopotentials. The Ceperly-Alder functional was used to approximate the exchange-correlation term.[20] This method has been extensively and successfully used to study many properties of a variety of type I and II clathrates.[14,17,18,21] In those studies, the calculated properties were in good agreement with experiment. The effects of the generalized gradient approximation (GGA) correction to the LDA were examined by others for the pristine type II Si_{136} material and were found to be minor.[18]

The calculations are carried out as follows. First, using

TABLE I. Birch-Murnaghan equation of state parameters ($T=0$ K) obtained from a fit of the LDA energy vs volume curve and the total binding energy per fcc unit cell for $Na_{16}Rb_8Si_{136}$, $K_{16}Rb_8Si_{136}$, and Si_{136}. Also listed are the available experimental parameters for Si_{136} obtained at $T=298$ K (Refs. 25 and 26).

Clathrate	E_0 (eV/atom)	V_0 (Å³/atom)	K (GPa)	K'	Total energy/fcc unit cell (eV)
$Na_{16}Rb_8Si_{136}$	−5.34	19.59	81.88	1.79	−213.56
$K_{16}Rb_8Si_{136}$	−5.33	19.78	86.17	0.51	−213.50
Si_{136}	−5.87	22.71	83.23	3.58	−199.73
Expt. Si_{136}	-	23.01	90	5.2	

VASP, we optimize the geometry of each compound by choosing a fixed lattice constant and relaxing the internal coordinates through a conjugate gradient algorithm using atomic forces. The process is repeated for several different lattice constants until the global minimum energy is found. Brillouin zone integrations were performed using a $4\times4\times4$ Monkhorst-Pack k-point grid.[22] Once the equilibrium lattice geometry is obtained for each material, the resulting LDA energy versus volume curve is fit with the Birch-Murnaghan equation of state (EOS).[23] This fitting determines the minimum binding energy E_0, the corresponding volume V_0, the equilibrium bulk modulus K, and its pressure derivative $K'=dK/dP$. Then, using VASP, the electronic band structures and densities of states are calculated for the optimized geometry by generating a separate set of k points along certain high symmetry directions in the Brillouin zone.

III. RESULTS AND DISCUSSION

The total LDA energies at various volumes were fitted to the Birch-Murnaghan equation of state, as just described.[24] The results for the fitting parameters E_0, V_0, K, K', and the total binding energy per fcc unit cell are listed in Table I for Si_{136}, $Na_{16}Rb_8Si_{136}$, and $K_{16}Rb_8Si_{136}$. Experimental values of some of the parameters for Si_{136} are also listed.[25,26] As expected, the predicted total binding energy per fcc unit cell for the filled clathrates is higher than that for the guest free Si_{136}. Table II shows the calculated and experimental values of the lattice constants for Si_{136} and $Na_{16}Rb_8Si_{136}$ (Refs. 2 and 15) and also the calculated value for $K_{16}Rb_8Si_{136}$. These are in excellent agreement with experiment. The equilibrium volume for $Na_{16}Rb_8Si_{136}$ gives a cubic lattice constant of 14.63 Å, about 0.7% smaller than the experimental value of 14.738 Å.

The electronic band structure and density of states (DOS) calculations were done for the clathrates at their optimized

TABLE II. Calculated and experimental values of the lattice constants for $Na_{16}Rb_8Si_{136}$, $K_{16}Rb_8Si_{136}$, and Si_{136} clathrates (Refs. 2 and 15).

Clathrate	Calculated (Å)	Experiment (Å)
$Na_{16}Rb_8Si_{136}$	14.63	14.738
$K_{16}Rb_8Si_{136}$	14.64	-
Si_{136}	14.56	14.626

geometries. It is well known that the LDA underestimates the minimum energy band gaps. However, it has been shown to predict energy differences and trends correctly, so a comparison of the band gaps between clathrates should be meaningful.[27]

Figures 1(a)–1(c) show the predicted electronic band structures for the three materials. To enable an easy qualitative comparison, for each material we have chosen the zero of energy at the top of the valence band. The pristine material, Si_{136}, has a predicted indirect band gap of about 1.24 eV, in agreement with LDA results obtained by others.[18,28] The results for $Na_{16}Rb_8Si_{136}$ and $K_{16}Rb_8Si_{136}$ are nearly identical to those of the parent Si_{136} clathrate. For the filled clathrates, there is a "pseudogap" between the top of the valence band and the bottom of the conduction band at the L point. For $Na_{16}Rb_8Si_{136}$, this is found to be approximately 0.75 eV or about 0.5 eV smaller than the LDA gap found for Si_{136}. The results also show that the pseudogap for $K_{16}Rb_8Si_{136}$ stays nearly the same as the bandgap of Si_{136}. For this material, we also predict an overall decrease in the gap between the conduction and valence bands at various Brillouin zone points.

Since all host framework bonds are satisfied by the Si valence electrons, electrons from the guests occupy the conduction states of the parent Si_{136}. The Fermi levels for the filled clathrates lie within the Si_{136} conduction band, as shown in Figs. 1(b) and 1(c). Our results agree qualitatively with the "rigid-band model,"[14,29] which predicts that the bands for the guest-containing materials are nearly the same as those of the framework and that there is a charge transfer from the guests into the host conduction states. This raises the Fermi level into the conduction band. The band structure results for $Na_{16}Rb_8Si_{136}$ are consistent with the metallic behavior reported for that material by Latturner et al.[15]

Figure 2 shows the predicted electronic densities of states (DOS) for Si_{136}, $K_{16}Rb_8Si_{136}$, and $Na_{16}Rb_8Si_{136}$. The DOS distribution near the Fermi level of the filled clathrates shows a charge transfer from the Na (or K) and Rb atoms to the Si framework. The DOS near the Fermi level is higher for the filled clathrates, because the guest atoms donate electrons to the Si framework. This increase might be associated with the low-temperature metallic behavior observed in $Na_{16}Rb_8Si_{136}$.[15] Comparison of the DOS for the three materials shows that there is a dip in the DOS near the Fermi levels of $K_{16}Rb_8Si_{136}$ and $Na_{16}Rb_8Si_{136}$. Such a dip was not found in theoretical studies of some other filled type II clathrates such as Cs_8Ge_{136}.[30]
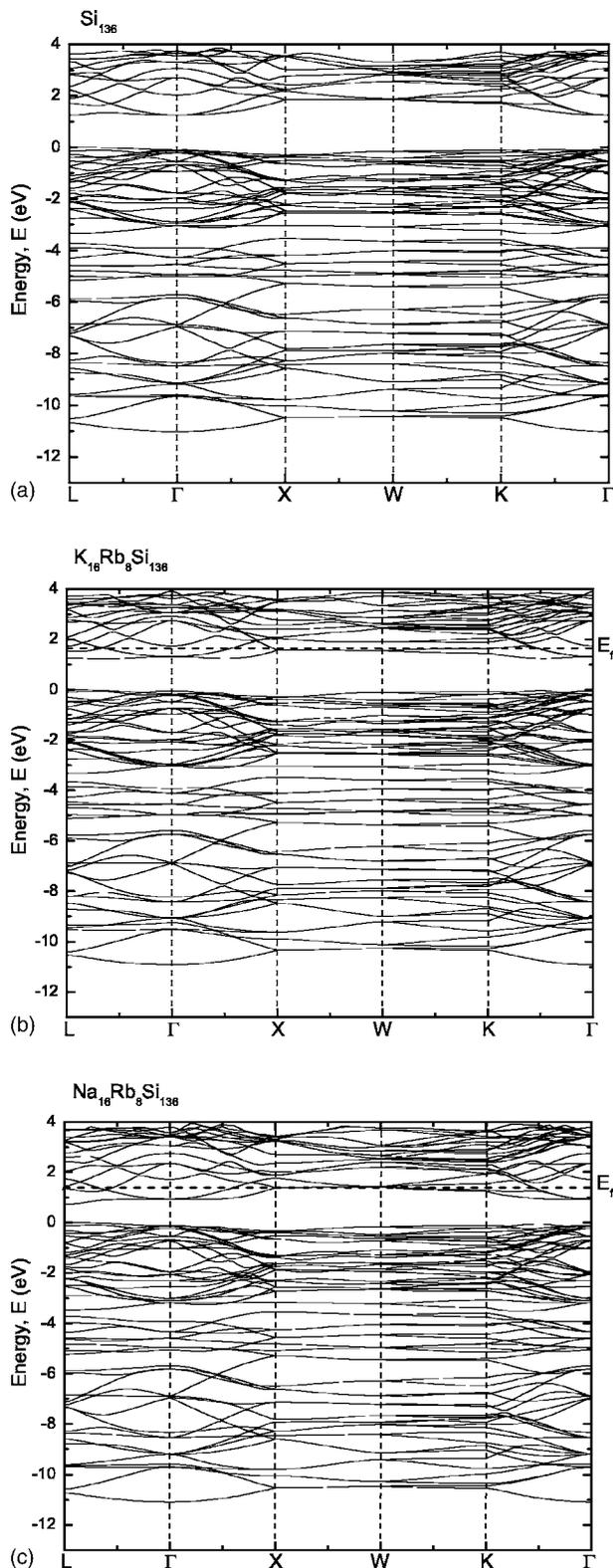
FIG. 1. Electronic band structure of (a) Si$_{136}$, (b) K$_{16}$Rb$_8$Si$_{136}$, and (c) Na$_{16}$Rb$_8$Si$_{136}$. In all figures, the top of the valence band is the zero of energy. In (b) and (c), the Fermi level is pushed into the conduction band as shown by a dashed line at ≈1.6 and 1.4 eV, respectively.
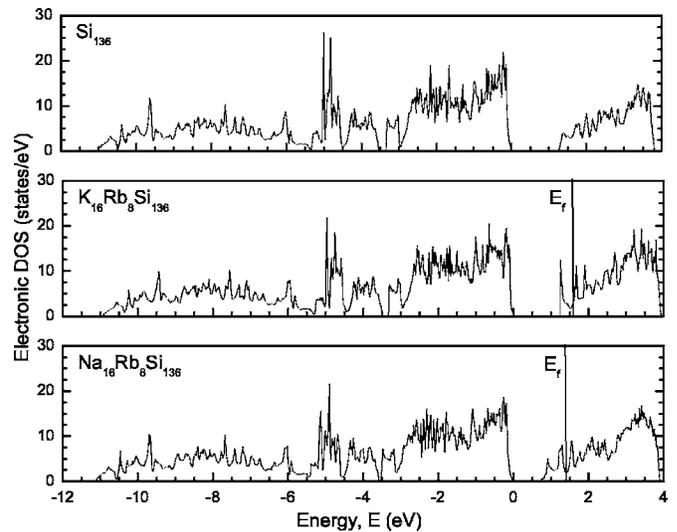
FIG. 2. Electronic density of states of Si$_{136}$, K$_{16}$Rb$_8$Si$_{136}$, and Na$_{16}$Rb$_8$Si$_{136}$ in the valence band and the lower portion of the conduction band. The Fermi levels of K$_{16}$Rb$_8$Si$_{136}$ and Na$_{16}$Rb$_8$Si$_{136}$ are shown by a vertical line.

Large Knight shifts have been observed in NMR experiments in the Na$_{16}$Rb$_8$Si$_{136}$ and Na$_{16}$Cs$_8$Si$_{136}$ clathrates.[15,31] The alkali metal atoms in both materials are NMR active. In these type II clathrates, the Knight shifts for ^{23}Na, ^{87}Rb, ^{133}Cs, and ^{29}Si each increase with decreasing temperature. This strong temperature dependence is very different from the Knight shift observed in metals, where it is approximately temperature independent.[32] The temperature-dependent Knight shift observed in some of the clathrates may be attributable to two factors: a temperature dependent conduction electron spin contribution to the Pauli paramagnetic susceptibility χ_p and a temperature-dependent contribution from the magnitude of the s-component wave function at the nucleus $[|\psi_s(0)|]$.[33]

As originally proposed by Gryko *et al.*,[16] contributions from these two sources may be related to a structural feature of the electronic DOS, which is not generally seen in metals. This consists of sharp peaks near the Fermi level (E_f), separated by an energy difference, ΔE. As is shown in Fig. 3, our results are consistent with this description. They clearly show two narrow peaks, separated by a ΔE near the Fermi level in both Na$_{16}$Rb$_8$Si$_{136}$ and K$_{16}$Rb$_8$Si$_{136}$. This "dip splitting" in the conduction band of these filled clathrates is probably because the electronic wave functions of the conduction band states of the framework material are not greatly affected by the presence of the guest atoms inside the cages. However, the energy spacings of these bands are considerably affected near the Fermi level, leading to the two-peaked structure of the DOS, as seen in Fig. 3. This sharp dip in the DOS near the E_f of the filled clathrates may provide a qualitative explanation for the observed large temperature-dependent Knight shifts.

Figure 4 shows the s and p-orbital projected density of states (p-DOS) of the three alkali atoms, the Na and the K located in the 20-atom cage, and the Rb inside the 28-atom cage. It clearly shows the s-orbital character of the states
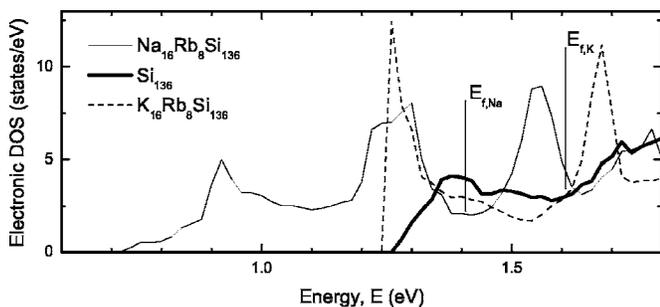
FIG. 3. Comparison of density of states of Si_{136}, $Na_{16}Rb_8Si_{136}$, and $K_{16}Rb_8Si_{136}$ in the lower portion of the conduction band. Fermi levels for $Na_{16}Rb_8Si_{136}$ and $K_{16}Rb_8Si_{136}$ are shown as $E_{f,Na}$ and $E_{f,K}$, respectively. The latter two show a dip in DOS near the Fermi level.

near E_f. Judging from the p-DOS of the three alkali metals, we predict that the lower of the two peaks near the Fermi level in Fig. 3 will be similar to an impurity derived donor-like band. If the separation between these two peaks (ΔE) is approximately in the range of k_BT at the experimental temperatures, then this model might help us understand the temperature dependence of the Knight shift observed in these clathrates. At high temperatures, thermal excitation could promote electrons from the narrow alkali states to the p-like framework states. This thermal promotion across the "dip" of the two-peaked structure in the DOS will generally lead to an Arrhenius-like behavior of the susceptibility and Knight shift at higher temperatures. At low temperatures, however, the electrons are more likely to be found in the s-like donor bands. As the electrons become more confined to the low-lying donor bands at low temperatures, the magnitude of the s-component wave function at the nucleus $[|\psi_s(0)|]$ increases, resulting in an increase in the Knight shift.[33] The relatively high, narrow peaks of the DOS also mean a complicated electronic distribution, which may vary with changing temperature. Hence, a variation in χ_p, which also depends on the electronic configuration near the Fermi level, is also expected to have a temperature variation.

IV. CONCLUSIONS

We have used the LDA to study the equations of state and the electronic structures of the type II clathrate materials Si_{136}, $Na_{16}Rb_8Si_{136}$, and $K_{16}Rb_8Si_{136}$. Our results are consistent with the rigid-band model. The band structure of
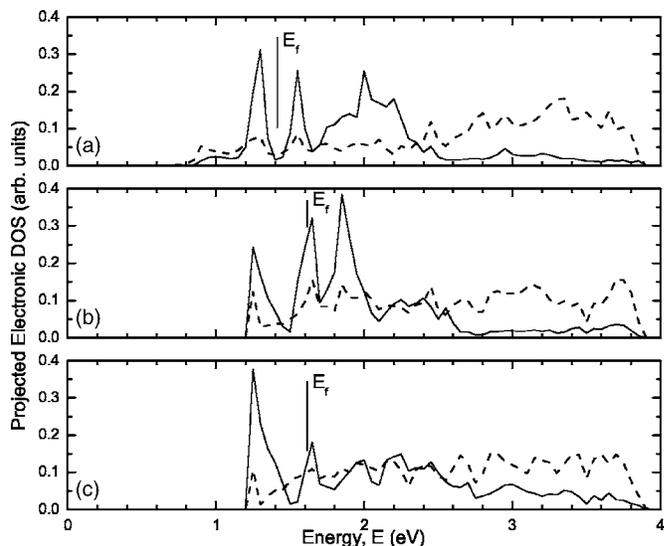
FIG. 4. s (solid line) and p-orbital (dashed line) projected density of states for (a) Na, (b) K, and (c) Rb in the lower portion of the conduction band near the Fermi level.

$Na_{16}Rb_8Si_{136}$, with a predicted LDA "pseudogap" of 0.75 eV, is in qualitative agreement with the observed metallic behavior of this material at low temperatures.[15] The densities of states show a dip near the Fermi level. Furthermore, the p-DOS of the three alkali metals show the s-orbital character of the states near E_f. For the filled clathrates, this is consistent with the temperature-dependent Knight shift observed in NMR of some of these materials. Unlike metals, which have a broad, featureless DOS at the Fermi level, we predict that these filled clathrates should have a highly structured DOS in that region, which causes the observed temperature dependent change in the electronic configuration and provides a qualitative explanation for the temperature-dependent Knight shift.

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