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Electronic structure of Si and Ge gold-doped clathrates

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The electronic properties of single phase type-I clathrate compounds, $Ba_8Au_6(\mathrm{Si\ or\ Ge})_{40}$ and Ba_8Ge_{46-x} have been investigated. The crystal structure, electrical resistivities, magnetic susceptibilities, the density of states at the Fermi level, and the band gap (where applicable) were determined. $Ba_8Au_6Si_{40}$ and $Ba_8Au_6Ge_{40}$ show a metallic behavior whereas Ba_8Ge_{46-x} is semiconducting. On a basis of this work, a first evidence is presented of the existence of type-I mixed-clathrates containing both silicon and germanium.
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Clathrates, which are essentially extended Si and Ge fullerene solids,[1,2] have been drawing considerable interest during the past few years. The doping of clathrates has opened a field of new nano scale materials with a wide variety of properties ranging from insulators to metals, e.g. Refs. 3 and 4. Some clathrates exhibit superconductivity when doped with alkaline-earth metals, e.g., Ba.[5–8] Unlike the intercalated fullerides, doped clathrates are air-stable because dopants reside inside the Si or Ge cages (endohedral). Clathrates with two distinct structure types have been reported.[1] A type-I clathrate with the general chemical formula of $M_x(\mathrm{Si\ or\ Ge})_{46}$ (M=alkali or alkaline-earth) has a A15 unit cell (space group $Pm\overline{3}n$). Two Si_{20} or Ge_{20} fullerenes per cell are located at the corner and the body-center positions and are connected covalently by six additional Si or Ge atoms on the faces of the unit cell (crystallographically, the 6*c* site, see Table I for unit cell parameters).[9,10] The structure can accommodate at maximum eight endohedral atoms.

It was shown that the Si or Ge atoms (at the 6*c* positions) bridging the $(\mathrm{Si\ or\ Ge})_{20}$ fullerenes can be replaced by transition metals,[9] and the extent of substitution depends on the metal used. It can be expected that unique electronic properties will be achieved in the future by regulating the 6*c*-site elements. The electronic properties of the clathrates are expected to depend on the nature and the extent of metal substitution. The localization/delocalization of electrons could be controlled by them. Hopefully, strong interactions between magnetic spins of the substituting metal and conduction electrons spreading into the network of clathrates may also be obtained. Hence, it is important to study the effects of metal substitution on the electronic properties of the clathrates. In this paper, we report the electronic properties of Au-doped Si and Ge clathrates.

The clathrates were produced by direct reaction of the stoichiometric amounts of the elements in a RF-induction furnace. Under inert gas atmosphere, Ge or Si and gold were first placed on a copper crucible and finally a barium sheet was placed on top. The mixture was quickly melted (<1 min) by RF-induction heating, held at the liquid state for ~30 second and was then cooled down to room temperature in less than 2 min. The formation of the Ge clathrates is found to be strongly exothermic while $Ba_8Au_6Si_{40}$ is exothermic to a minor extent.

The products were analyzed by transport measurements, superconduction quantum interference device (SQUID), powder x-ray diffraction (XRD) and electron diffraction. Resistivity was determined from 4 to 300 K by applying a constant current (1, 10, and 100 mA) across an ingot sample and measurement of the voltage between two points on the sample surface. The susceptibilities χ_{total} obtained from SQUID were fitted to different mathematical functions ac-

TABLE I. Unit cell parameters for type-I clathrates [$M_x(\mathrm{Si\ or\ Ge})_{46}$, M=alkali metal or alkaline earth, space group $Pm\overline{3}n$].

Site	Occupation	x	y	z
2*a*, endohedral	M	0	0	0
6*d*, endohedral	M	0.25	0.5	0
6*c*	Si or Ge	0.25	0	0.5
16*i*	Si or Ge	0.183	0.183	0.183
24*k*	Si or Ge	0	0.31	0.166

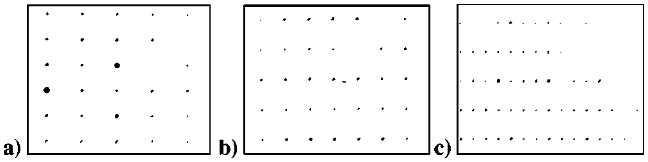

FIG. 1. Electron diffraction measurement of (a) $Ba_8Au_6Si_{40}$, [211] direction and of (b) $Ba_8Au_6Ge_{40}$, [110] direction (c) Ba_8Ge_{43}, [211] direction. The patterns (a) and (b) show a regular cubic lattice; (c) shows a superlattice with twice the lattice constant.

cording to the types of conductors formed (semiconductors, metals etc.) The XRD patterns were analyzed by intensity calculations (using the XLAZY-PULVERIX program) and Rietveld refinement using, e.g., the Cerius^2 program package.

The XRD results and electron diffraction measurements showed that single-phase $Ba_8Au_6(Ge\text{ or }Si)_{40}$ clathrate compounds were formed. The electron diffraction patterns showed a cubic lattice with no superlattice peaks in the [100], [110], and [211] directions [see Fig. 1(a) for [211] of $Ba_8Au_6Si_{40}$ and Fig. 1(b) for [110] of $Ba_8Au_6Ge_{40}$]. Intensity simulation [based on the space group $Pm\overline{3}n$ and the unit cell parameters of Na_8Si_{46} (Ref. 1)] confirmed that in these compounds all the Si or Ge atoms at the 6*c* sites (total of six per cell) have been substituted by Au atoms, and all the endohedral positions (2*a* and 6*d*) are occupied by Ba atoms. The measured lattice constants are 10.80 (4) Å and 10.42 (4) Å (the value in parenthesis represents the error in the last digit), which agree within the errors with the literature values.[9]

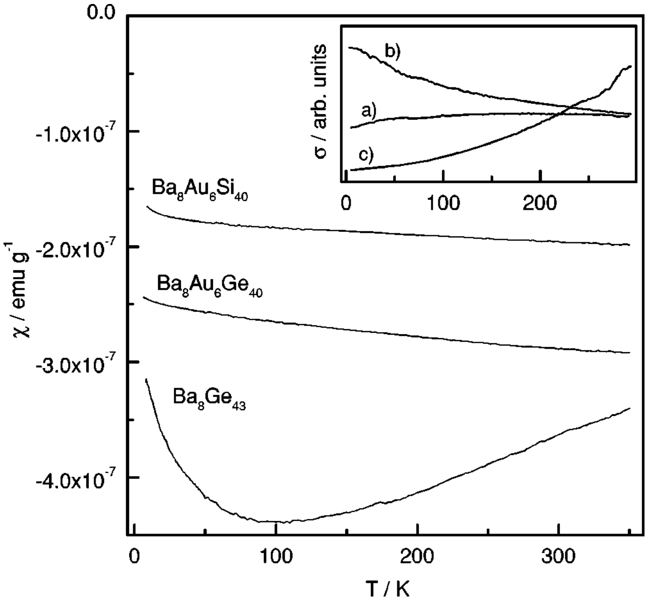

FIG. 2. Total susceptibility versus temperature obtained by SQUID analysis for $Ba_8Au_6Si_{40}$ (a), $Ba_8Au_6Ge_{40}$ (b), and Ba_8Ge_{43} (c). The third curve shows a strong semiconducting behavior. The inset shows the conductivity versus temperature adjusted to fit the figure for these three compounds in arbitrary units.

The resistivities of both gold inclusion compounds were measured from 4 to 300 K. The resistivities were found to be in the order of 10^{-4} and 10^{-5} Ωm at 300 K for the Si and Ge clathrates, respectively. The temperature dependence results show that they are metallic (see inset of Fig. 2). The total susceptibility (χ_{total}) of both compounds were measured by SQUID. The data can be interpreted using a nearly temperature-independent part (χ_{lin}) and a Curie-like temperature-dependent part (χ_{Curie}) (see Fig. 2). Both compounds have a similar Curie term with spin densities of about 0.1% per unit, which can reasonably be attributed to the defect spins in the crystals. The sum of the diamagnetic (χ_{dia}, negative) and the Pauli type (χ_{Pauli}, positive) susceptibility (χ_{lin}) was determined to be $\chi_{lin}=-2.51(2)\times10^{-7}$ emu/g and $\chi_{lin}=-1.78(2)\times10^{-7}$ emu/g for $Ba_8Au_6Ge_{40}$ and $Ba_8Au_6Si_{40}$, respectively. In order to estimate $\chi_{Pauli}=\chi_{lin}-\chi_{dia}$ the reported χ_{dia}^{lit} values[11] of the different atoms in the clathrate phases were added. This results in a $\chi_{dia}^{lit}=-1.71\times10^{-7}$ emu/g for $Ba_8Au_6Ge_{40}$ and $\chi_{dia}^{lit}=-1.67\times10^{-7}$ emu/g for $Ba_8Au_6Si_{40}$. These values give negative χ_{Pauli}'s which are inconsistent with any physical picture. Other effects have to be considered for a reasonable estimate of the χ_{dia}. Some geometric contributions to χ_{dia} in $Ba_8Au_6Ge_{40}$ would be similar to those in Ba_8Ge_{4x} because of the very similar crystal structure. Thus using the experimentally observed χ_{dia} of Ba_8Ge_{43} (described later) and correcting it for the appropriate gold contents, χ_{dia} of $Ba_8Au_6Ge_{40}$ can be estimated to be $-4.1(3)\times10^{-7}$ emu/g.

Ramirez *et al.*[12] have observed a similar deviation of χ_{dia} in C_{60} and carbon tubules. They attribute this to the ring currents on the cages and suggested Pauling's formula for Lamor diamagnetism.

$$\chi_{\pi}=-60(e^2/4m_ec^2)4.09\times l^2, \tag{1}$$

where e and m_e are the charge and the mass of an electron, c is the speed of light, and l is the bond length. This model would also be valid for the clathrates discussed here if the electrons transferred from the Ba atoms modify the hybridization of the Ge_{20} orbitals in a way similar to the π orbitals in C_{60} leading to weak orbital-ovelapping between the $(Si\text{ or }Ge)_{20}$ cage atoms (16*i* and 24*k*) and the atoms (6*c*). Using this simple model and assuming that each Ba atom donates an average of 1.5 electrons (described later) a $\chi_{ring}=-2.41\times10^{-7}$ emu/g would be added, yielding $\chi_{dia}=-4.12\times10^{-7}$ emu/g, which is in good agreement with our value.

Applying this model also to the Si-based clathrates the values of $\chi_{ring}=-3.40\times10^{-7}$ emu/g and $\chi_{dia}=-5.07\times10^{-7}$ emu/g are deduced. Since Ba_8Si_{46} cannot be synthesized from the melt for reasons of competing reactions forming $BaSi_2$, the χ_{dia} was determined from a semiconducting $Ba_8Cu_4Si_{42}$ sample after a correction for the gold contents to be $\chi_{dia}=-3.2\times10^{-7}$ emu/g. This experimental value is much higher than the one obtained from the model. This could be an indication for a lower degree of ionization of the Ba ions in the case of Si clathrates. On the other hand, a simple model like the one suggested by Ramirez *et al.* might need further corrections as well.

From these susceptibilities experi χ_{Pauli} values can be determined to be $+1.6\times10^{-7}$ emu/g and 1.42×10^{-7} emu/g, respectively, which are equivalent to a density of states at the Fermi level (N_{E_F}) of 13(1) and 7(3) per eV for $Ba_8Au_6Ge_{40}$ and $Ba_8Au_6Si_{40}$, respectively. However, other mechanisms might change χ_{dia}, and the values given here might need further correction. These extracted values are fairly small, when they are compared to those of the superconducting $Na_2Ba_6Si_{46}$ clathrate,[8] and seem to show that the gold inclusion clathrates studied here are weak metals. Actually neither compound showed any superconductivity down to 2 K.

To study the influence of gold substitution, a nominal Ba_8Ge_{46} was prepared using the RF induction method. Temperature-dependent resistivity measurements showed that Ba_8Ge_{46} is semiconducting. From the magnetic susceptibility measurements electronic properties have also been studied. The main contribution in the susceptibility shows a semiconducting behavior, this confirming the results of the resistivity measurements.

In order to elucidate the observed differences between the pure Ba-inclusion Ge and the Au-containing Ba-(Si or Ge) clathrates, the structure of the nominal Ba_8Ge_{46} clathrate has been studied in detail. Rietveld analyses of the XRD pattern of the nominal Ba_8Ge_{46} clathrate implies that some Ge on the 6*c* sites are missing, but this is not the case for the Au-doped Ba-(Si or Ge) clathrates.[13] According to these investigations the favorable stoichiometry is Ba_8Ge_{43} which is equivalent to three missing Ge atoms per unit. Thus, 3×4 dangling bonds have to be saturated. This leeds to an average degree of 1.5 electron transfer of the 8 Ba atoms. Similar defects were also observed for other clathrates, e.g., K_8Ge_{44} by Cordier *et al.*[9] Electron diffraction patterns of Ba_8Ge_{43} show superlattice peaks [see Fig. 1(c)], supporting such an idea. Considering the fact that the period of the superlattice peaks is twice the lattice constant, it is likely that the superlattice is made due to the missing of half the Ge elements on the 6*c* positions connecting the Ge_{20} clusters.

The band gap of the nominal Ba_8Ge_{46} was determined by transport measurements to be 40 (4) meV (see inset of Fig. 2). SQUID analysis revealed similar magnetic susceptibilities for samples prepared as nominal Ba_8Ge_{43} and as nominal Ba_8Ge_{42} (see Fig. 2 for the nominal Ba_8Ge_{43}) with a band gap of 42(2) meV being in good agreement with the transport result. The diamagnetic susceptibility was determined to be $-4.8(3)\times10^{-7}$ emu/g. The Curie constant of about $2.5(3)\times10^{-6}$ emu/g yields a spin defect density of 3% per molecule. The value is much higher than the one for gold inclusion compounds and supports that the Ba_8Ge_{43} sample has a deviation from the ideal Ba_8Ge_{46} structure with defects, which would consequently imply that the occupation of transition metals on the 6*c* positions could stabilize of the type-I clathrate formation.

The enhanced stabilization of type-I clathrates by Au at the 6*c* position has suggested us to try having a chance to synthesize a type-I clathrate with a framework of both silicon and germanium, which is difficult to make under conventional conditions. Although much useful information has hitherto been accumulated in the field of clathrates with either a Si or Ge framework to date, to the best of our knowledge no successful studies have been published dealing with the possibility of Si-Ge binary-framework clathrates. Since Ge and Si behave with large differences in formation of clathrates at low-doping levels of transition metals into the 6*c* positions, it shall be of great interest to see whether such binary-framework clathrates can be achieved.

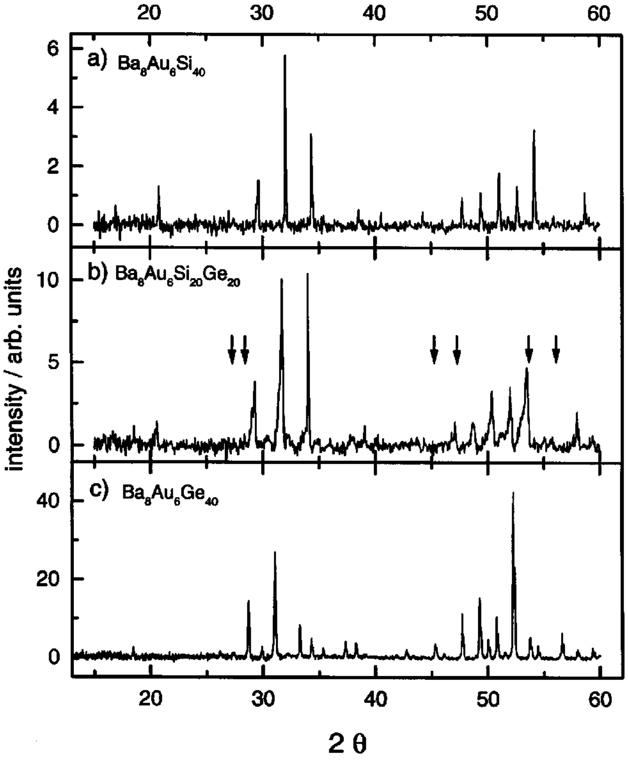

FIG. 3. XRD spectrum of (a) $Ba_8Au_6Si_{40}$, (b) the nominal $Ba_8Au_6Si_{20}Ge_{20}$ and, (c) $Ba_8Au_6Ge_{40}$. The line positions of pristine Si and Ge are indicated by arrows.

The XRD pattern of the nominal $Ba_8Au_6Si_{20}Ge_{20}$ compound showed that an expected clathrate has been synthesized with a lattice constant of 10.57 Å. The XRD spectrum is shown in Fig. 3(b). The fact that the peaks in the XRD spectrum are so sharp shows that a major phase is present consisting of mixed $(Si,Ge)_{20}$ cages. The lines in this spectrum, however, are shaded to lower angles to a small extent, indicating that the lattice is not overall homogeneous but has some parts with slightly larger lattice constant. It is interesting to note that there are neither signals from pristine Si or Ge (reflections of pristine Si and Ge are marked by arrows in Fig. 3(b) nor from the nonmixed clathrates visible in the spectrum [see Fig. 3(a) for $Ba_8Au_6Si_{40}$ and Fig. 3(c) for $Ba_8Au_6Ge_{40}$].

In conclusion, the addition of gold to the $Ba_8(\text{Si or Ge})_{4x}$ clathrates produces metallic samples that have the ideal $Ba_8Au_6(\text{Si or Ge})_{40}$ stoichiometry with no lattice sites unoccupied. On the other hand, when trying to occupy the 6*c* sites with Ge under ambient pressure, only up to half of these sites are occupied[14] leading to semiconductivity in the resulting Ba_8Ge_{43} with superlattice structure. These results confirm the already published interpretation that the Ba atoms are ionized to a degree of less or equal to 2 and the additional electrons are localized at the 6*c* sites reducing the available bonds. It was shown that the occupation of the 6*c* sites largely modifies the electronic states of these clathrates. Thus, it will be interesting to see in the future how elements baring a magnetic spin at the 6*c* locations interact with the conduction electrons.

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