Superconductivity in germanium clathrate $Ba_8Ga_{16}Ge_{30}$

J. D. Bryan, V. I. Srdanov, and G. D. Stucky

Department of Chemistry, University of California, Santa Barbara, California 93106

D. Schmidt

Department of Physics, University of California, Santa Barbara, California 93106

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We report type-II superconductivity in the germanium clathrate compound, $Ba_8Ga_{16}Ge_{30}$ with critical temperature, $T_c = 7.5 \pm 0.2$ K as determined by magnetic susceptibility measurements. Barium atoms occupy cage voids provided by a covalent sp^3 hybridized network of gallium and germanium. Magnetic susceptibility and transport measurements were used to characterize the transition. [S0163-1829(99)06829-0]

Following the pioneering work of Pauling and Marsh on the $[CL_2]_6(H_2O)_{46}$ clathrate structure,[1] a number of isostructural clathrate compounds have been discovered. Common to all of them is a simple cubic (sc) lattice whose crystallographic cell is made out of 46 tetrahedral linked atomic or molecular units. These framework species T form cagelike voids of high symmetry in which another type of atomic or molecular species are encapsulated. Unlike fullerenes, clathrate cages are face sharing thus giving rise to an expanded framework similar to zeolites. The particular M_xT_{46} clathrate features two types of cages, shown in Fig. 1. The smaller, 20 atom cage, is a dodecahedron [Fig. 1(a)] whereas the larger, 24 atom cage, is a tetrakaidecahedron [Fig. 1(b)]. There are two smaller and six larger cages in the unit cell, which do not all need to be occupied; i.e., $8 \leq x$. Cros and co-workers[3-6] synthesized covalent clathrate frameworks out of sp^3 hybridized group IV elements, which featured encapsulated alkali-metal atoms. Na_8Si_{46} and K_7Si_{46} clathrates were dubbed metallic[7] despite relatively small and temperature-independent dc conductivity. Structural defects and poor Ohmic contacts at the grain boundaries were held responsible for high resistivity and the anomalous temperature dependence in these compounds.[7] Eisenmann and co-workers[8] extended the clathrate class in the 1980's to encompass alkaline-earth elements with formula $(II)_8(III,IV)_{46}$. More recently, Ba atoms were successfully encapsulated inside the clathrate cages composed of silicon, giving rise to mixed $(I,II)_x(IV)_{46}$ clathrates.[9-11] The clathrate $(Na,Ba)_xSi_{46}$ was found superconducting below 4 K.[12] Like its alkaline-only relatives, $(Na,Ba)_xSi_{46}$ clathrate shows temperature-independent conductivity above T_c. Its metallic nature, however, was confirmed by the recent NMR studies[13,14] in which temperature-independent, Knight-shifted ^{137}Ba resonance was found to satisfy the Korringa relation. It has been proposed that Ba states are hybridized with those forming the conduction band of the Si_{46} framework, yielding an increased density of states at the Fermi level. The latter is held responsible for the occurrence of superconductivity in the barium-containing compound, in accordance with the BCS formalism.

In a response to the quest for better thermoelectric materials[15,16] we recently engaged in a synthesis of various $(I,II,)_x(III,IV)_{46,1136}$ clathrates. Some of them were found to be superconducting at low temperatures, thus providing us with a rare opportunity to address correlations between composition and the transition temperature in a series of isostructural compounds. The first in the series to be described is $Ba_8Ga_{16}Ge_{30}$ clathrate which exhibits type-II superconductivity with the $T_c = 7.5 \pm 0.2$ K.

The clathrate sample was prepared using a procedure adapted from Ref. 10. All manipulations of raw materials were performed in a high-purity argon-filled drybox. Stoichiometric amounts of the elemental starting materials (Cerac, 99.99%) were placed in a corundum crucible (Coors Inc.). The crucible was set inside a stainless-steel bomb sealed with a copper gasket. The mixture was heated at
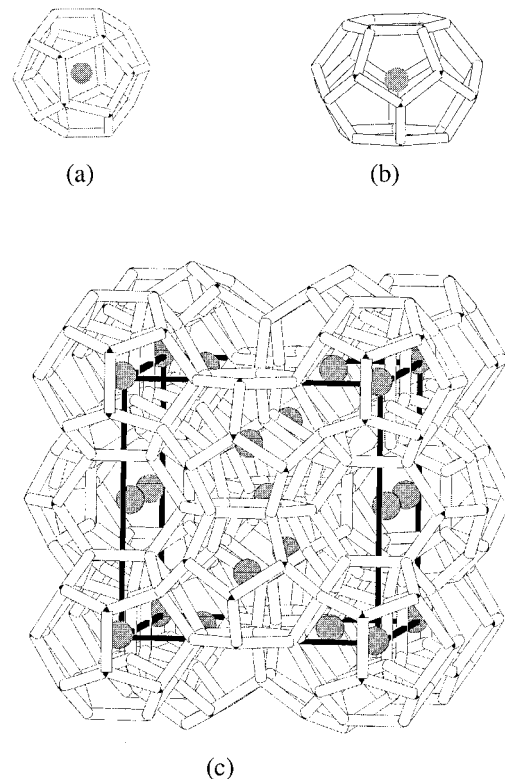

(a)   (b)

(c)

FIG. 1. (a) Smaller pentagonal dodecahedron with barium atom inclusion. (b) Larger tetrakaidecahedron with barium inclusion. (c) Extended single unit cell showing connectivity of cages.
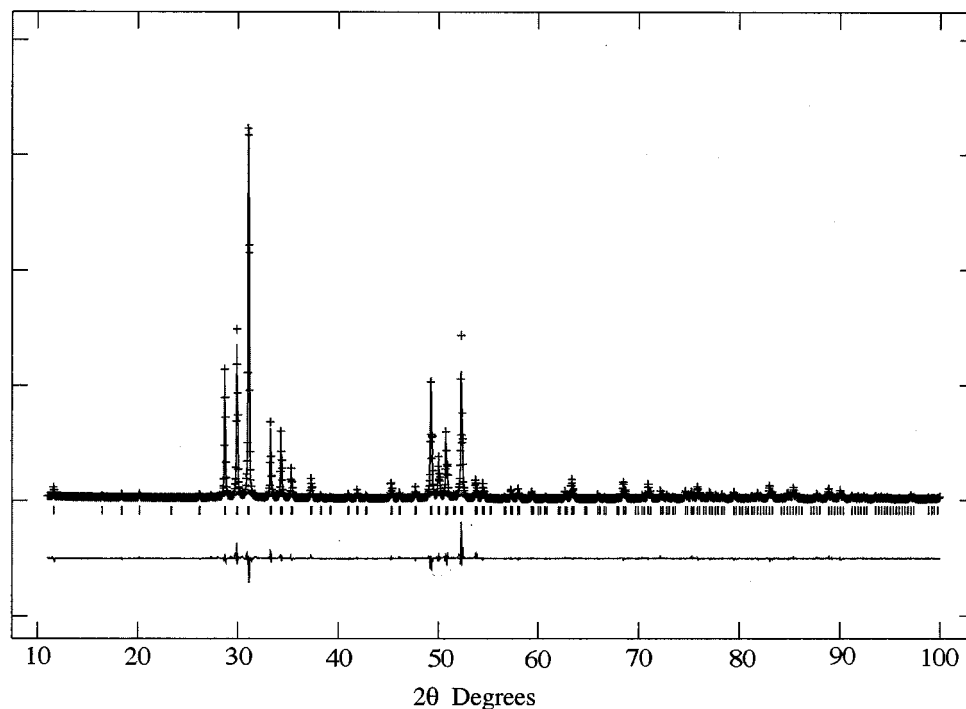
FIG. 2. Powder-diffraction pattern with Rietveld analysis and corresponding difference plot.

4.4 °C/min to 1080 °C, held for 1 h then cooled at 0.8 °C/min to 875 °C. The reaction was further cooled at 2.3 °C/min to room temperature. Inductively coupled plasma emission spectroscopy was used to determine composition of 23.49% Ba, 27.10% Ga, and 46.81% Ge by weight giving a stoichiometry of $Ba_{7.62}Ga_{17.30}Ge_{28.70}$. The x-ray powder-diffraction pattern, shown in Fig. 2, fully indexes in the $Pm\text{-}3n$ (O_h^3) space group with no extra reflections of any kind left unaccounted for. The absence of any supercell peaks implies that the Ga distribution throughout the Ge framework is random. Rietveld analysis on an idealized $Ba_8Ga_{16}Ge_{30}$ stoichiometry using GSAS software[17] was straightforward yielding $wR_p = 0.0986$ and $a_0 = 10.784\,40(9)$.

As one would expect, the heteroatom Ge-Ga framework shows a slightly larger average bond length than Ge-Ge bonds of the diamond structure, 2.51(2) and 2.45, respectively. While both structures are sp^3 hybridized the group IV clathrate class of compounds show a large distribution of bond lengths and angles giving the structure a degree of flexibility toward substitutions.[18] Unfortunately, the powder-diffraction data did not allow refinement of the framework Ga/Ge ratio which was therefore held fixed, consistent with the results of elemental analysis. The Ba occupancy, however, was refined to the factors shown in Table I with other selected crystallographic parameters.

Magnetic measurements on finely ground bulk sample were made in the 1.8–300 K region by using a superconducting quantum interference device magnetometer Quantum Design, Model 1802. Figure 3 shows the susceptibility versus temperature for zero-field cooling (ZFC) and field-cooling (FC) runs for $Ba_8Ga_{16}Ge_{30}$ samples under a field of 10 G. The signal has been corrected for the diamagnetic core response from the constituent atoms.[19] The normalized susceptibility $4\pi\chi$ is used where χ has units of (emu/(G cm^3).

Here, the convention $1\,G\,cm^3 = 1$ emu resulting in a unitless number,[20] with a limiting value of -1 for a perfect diamagnet, was employed. The $T_c = 7.5$ K was approximated by the onset of a diamagnetic response. A critical field, H_{c1}, of 100 G was determined by measuring the magnetic moment in varying applied fields (not shown). The difference of the FC run from the ZFC run is often associated with the volume superconducting fraction or the percentage of Meissner phase.[20] Approximately 40% of the shielding expected for a perfect diamagnet was observed. It is important to note that this value is only the lower bound on the superconducting fraction as a consequence of a field penetration depth comparable to the particle size, determined by scanning electron microscope (SEM) to be on the order of 1–5 μm. Particle sizes near the order of the penetration depth often show an erroneous decreased superconducting fraction.[21]

As shown in Fig. 3, a second cusp or transition in the susceptibility occurs in the temperature run near 6 K. Although one cannot exclude a possibility for the coexistence of two superconducting clathrate stoichiometries, we offer an

TABLE I. Selected crystallographic parameters.

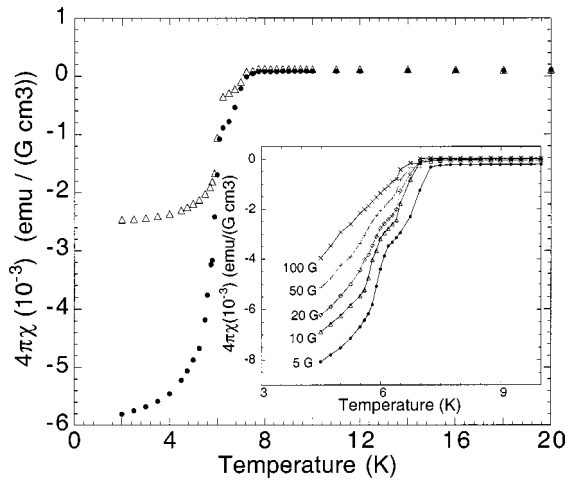| Atom	x,y,z	Fraction	Wykoff site and multiplicity
Ba	0,0,0,	0.9580(2)	$2a$
Ba	0.25, 0.5, 0	0.9769(1)	$6d$
Ga, Ge	0.25, 0, 0.5	1.0000	$6c$
Ga, Ge	x,x,x	1.0000	$16i$
	$x = 0.1855(1)$		
Ga,Ge	$0,y,z$	1.0000	$24k$
	$y = 0.3080(1)$; $z = 0.1185(1)$		

FIG. 3. $4\pi\chi$ vs temperature from 20 to 2 K for $Ba_8Ga_{16}Ge_{30}$, T_c estimated to be 7.5 K. ($\bullet$) denotes zero-field-cooling experiment, ($\triangle$) denotes the field-cooled experiment (inset) $4\pi\chi$ vs temperature plot for varying fields in a ZFC experiment. A slight shift in T_c observed for 100 G experiment is due to the nonlinearity of the moment response experienced near H_{c1}.

FIG. 4. Resistivity versus temperature from 20 to 2 K.

alternative explanation. The secondary transition may be associated with the decoupling of superconducting grains, as is similarly observed in the high-T_c cuprates.[20,22] The weakly superconducting grain boundaries sustain a lower critical current density than the corresponding bulk. Larger applied fields induced larger screening currents that eventually surpass the upper limit of the critical current density for these weakly superconducting regions, driving the grain decoupling to lower temperatures. Thompson and co-workers[22] showed that the critical temperature for decoupling of the superconducting grains is inversely proportional to the magnetic field in a ZFC experiment. As shown in the inset of Fig. 3, this is consistent with our experiment. We also note T_c in these experiments remains unchanged as long as the applied field is far below the critical field. We, therefore, conclude that the secondary transition is a direct result of decoupling of superconducting grains.

In the absence of single crystals, resistivity measurements were performed on samples pelletized under 1400 MPa. The pellet density was measured to be 87% of the theoretical density estimated from x-ray refinements. Figure 4 shows resistivity versus temperature for a $Ba_8Ga_{16}Ge_{30}$ with a critical temperature of approximately 4.8 K. A slight resistance enhancement was observed just prior to the transition. Standard ac techniques were used to measure the small signal resistivity in the temperature range from room temperature to 1.4 K with frequency of 100 Hz. Electrical contact was made with four spring-loaded contacts to form a van der Pauw geometry. A broad 10–90 % transition width of 2.4 K is observed. This broad transition is attributed to nonuniformity in the pellet, an artifact of cold pressing. We reconcile the discrepancy in the resistivity T_c compared to the T_c observed by susceptibility measurements by surface oxidation and nonstoichiometric surface sites in the polycrystalline grains. These sites serve as either nonsuperconducting or weakly superconducting regions, which have the effect of lowering the T_c.[23] This nonstoichiometry effect is documented[24] in the high-T_c copper oxide $La_{2-x}Sr_xCuO_{4-\delta}$,[25] where fluctua-

tions in T_c have been shown to be compositionally dependent upon x. It is then plausible to suggest that the T_c estimated through magnetic-susceptibility measurements is a measure of bulk intragrain superconductivity in our materials, while the resistivity measurements are more dependent on intergrain superconductivity. This suggestion is supported by the magnetic-susceptibility data, where complete flux expulsion from the sample is not seen until below 5 K, which agrees well with the resistivity data. A second cusp is also seen in the resistivity measurements, which agrees with the initial grain-boundary suggestions made from the magnetic data.
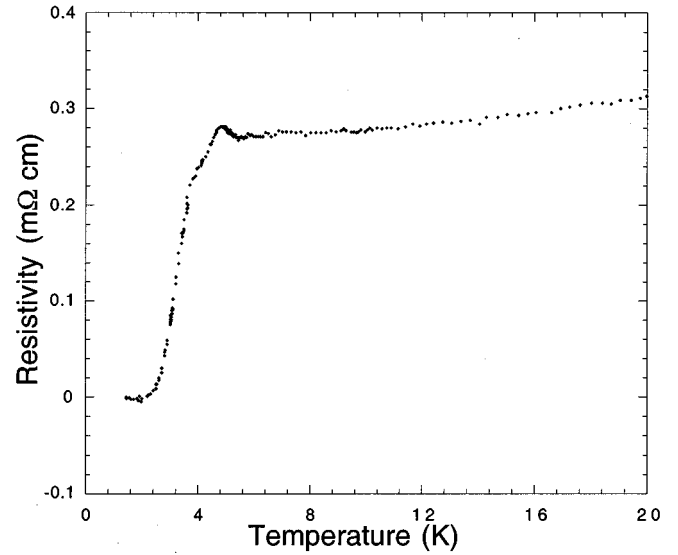
We note that the band-structure calculation of the hypothetical Si_{46} clathrate structure[2] predict a semiconductor with a fundamental gap of 1.26 eV. It is further believed that the valence electrons of encapsulated alkali metal are donated to the conduction band of such a clathrate, yielding metallic behavior in Na_8Si_{46} and K_8Si_{46}.[7] It is also proposed[2] that in the case of $(Na, Ba)_xSi_{46}$, s and d states of the alkaline-earth atom are mixed with those of silicon, thus giving rise to an enhanced density of states at the Fermi level, $N(E_f)$. The latter was used to explain the occurrence of superconductivity in $(Na, Ba)_xSi_{46}$, which is nonexistent in the pure alkali-metal clathrates. In the case of $Ba_8Ga_{16}Ge_{30}$, however; the partial Ga/Ge substitution creates an electron-deficient framework. In such a clathrate the encapsulated metal atoms must donate their electrons into the valence, rather than the conduction band of the hypothetical $III_{16}IV_{30}$ framework. Since $Ba_8Ga_6Ge_{30}$ clathrates show nearly metallic conductivity it must be that not all of the barium electrons are donated, thus leaving the clathrate ''valence'' band only partially filled. It would now be interesting to see whether the density-of-states calculations, coupled with premises of BCS theory, would help us rationalize superconductivity of such clathrates.

In summary, the low-temperature transport and magnetic susceptibility of the germanium-based clathrate $Ba_8Ga_6Ge_{30}$ were investigated. We observe superconductivity in this material with a T_c of 7.5 ± 0.2 K. Grain boundaries and nonsto-

ichiometric regions were shown to influence these measurements via a depression in transport T_c and the appearance of a second transition in the magnetic susceptibility. This discovery further emphasizes the rich physical and electronic structure of the group IV clathrates. Varying the framework composition and the choice of alkaline-earth element will likely lead to a broader understanding of their electronic properties and may yield insights into their thermoelectric behavior and potential for device application.

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