Ferromagnetism in Fe-doped Ba$_6$Ge$_{25}$ Chiral Clathrate

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We have successfully synthesized a Ba$_6$Ge$_{25}$ clathrate, substituting 3 Fe per formula unit by Ge. This chiral clathrate has Ge sites forming a framework of closed cages and helical tunnel networks. Fe atoms randomly occupy these sites, and exhibit high-spin magnetic moments. A ferromagnetic transition is observed with $T_c = 170$ K, the highest observed $T_c$ for a magnetic clathrate. However, the magnetic phase is significantly disordered, and exhibits a transformation to a re-entrant spin glass phase. This system has a number of features in common with other dilute magnetic semiconductors.

Si, Ge and Sn clathrates have received increasing attention over the past few years. These materials have a semiconducting framework into which metal atoms can be substituted, providing a number of possibilities for new materials for example new thermoelectrics and superconductors. Ferromagnetism has been observed in Mn-doped Ge clathrate, with $T_c = 10$ K and clathrates having Eu encapsulated in the cages, with $T_c$ up to 37 K. Currently there is strong interest in ferromagnetic semiconductors for spintronic applications and much effort has been devoted to the magnetic doping of semiconductors using low-temperature epitaxy. Clathrates offer the possibility of semiconducting phases containing magnetic atoms at equilibrium, which might be compatible with conventional substrates. Here, we report the synthesis of a stable Fe-doped Ge clathrate, and the observation of a ferromagnetic transition with $T_c = 170$ K.

Although several transition metals substitute for Ge in the type-I clathrate structure attempts at Fe substitution have failed due to competing Fe-Ge phases. However, we find that higher temperature synthesis produces a Fe-containing clathrate of the recently discovered chiral structure type, Ba$_6$Ge$_{25}$ Fe$_x$. This clathrate contains an open Ge-Ge bonded framework, threaded by closed dodecahedral cages. The material actually forms as Ba$_6$Ge$_{24}$, with vacancies occurring preferentially by a Zintl mechanism.

Our method followed several steps. Elemental mixtures, with excess Ba, were placed in BN crucibles, sealed under Ar, and pre-reacted by rf induction. The resulting mixtures included type-I clathrates and FeGe$_2$. Characterization was by x-ray diffraction (Bruker D8 Advance Powder, Cu Kα radiation), and refinement using GSAS software. To complete the reaction and eliminate FeGe$_2$, the mixtures were arc-melted several times in a water-cooled copper crucible. The ingots were then sealed in quartz ampoules and annealed at 700 °C for 100 hours. By this method we obtained single-phase or nearly single-phase Ba$_6$Ge$_{25-x}$Fe$_x$ with $x$ up to 3. However, furnace melting and slower cooling through the melting point produced a mixture of FeGe$_2$ and clathrate phases. An x-ray analysis for $x = 3$ is shown in Fig. 1A. All observed peaks were indexed according to the cubic space group P4$_3$32 (#213), as previously reported for Ba$_6$Ge$_{25}$ Fe$_x$. The lattice constant for $x = 3$ is $a = 1.45520$ nm, slightly larger than reported for Ba$_6$Ge$_{24}$ ($a = 1.45483$ nm). Energy-dispersive x-ray spectroscopy (EDS) and electron diffraction measurements (JEOL JEM-2010 electron microscope, 100 kV) for the $x = 3$ sample showed that Fe was indeed incorporated in the clathrate phase. These measurements also showed trace amounts of Ge and FeGe$_2$ to be present, but below the x-ray detectability limit (a few percent). Thus a minor fraction of the Fe atoms are present as FeGe$_2$. No other phases were observed. Analysis gave an average clathrate composition Ba$_6$Ge$_{21.9}$Fe$_{3.1}$ for the $x = 3$ sample, a Ge:Fe ratio close to the starting composition. The Fe content per formula unit was $3.1 \pm 1$, with variations observed between crystallites, however the crystallites appeared locally homogeneous, with no apparent clustering.

The chiral clathrate structure (Fig. 1B) has Ba situated in open channels as well as closed cages. In the Ge$_{25}$ framework, two of the six distinct sites have three Ge-Ge bonds, the others having four. By contrast, type I and II clathrates have only 4-bonded Ge sites in approximately tetrahedral bonding configurations, and closed cages. In our x-ray analysis we placed Fe predominantly on three of the six sites, similar to the occupation parameters for In-doped Ge$_{25}$ clathrate and the refinement gave a com-

FIG. 1: X-ray refinement for Ba$_6$Ge$_{22}$Fe$_3$. Upper curve: data with fit. Lower curve: difference plot. Ticks show peaks indexed according to the chiral clathrate structure. Unit cell with clathrate framework is inset, showing a distorted dodecahedral cage at lower left. 3-bonded sites shown as open circles.
position $\text{Ba}_6\text{Ge}_{21.8}\text{Fe}_{3.0}$, in excellent agreement with the EDS result ($\text{Ba}_6\text{Ge}_{21.9}\text{Fe}_{3.1}$). However, since the Fe and Ge x-ray structure factors are similar, we found that Fe could be redistributed among framework sites to give a similar composition and nearly identical goodness of fit ($R$ values: $R_{wp} = 0.077$ and $R_p = 0.053$). The specific Fe locations therefore are uncertain, although it is clear that they are distributed in the clathrate framework.

Magnetic measurements were made on a $\text{Ba}_6\text{Ge}_{22}\text{Fe}_3$ sample using a SQUID magnetometer (Quantum Design MPMS-XL). Zero-field-cooled (ZFC) magnetization was measured on warming in fixed field, while field-cooled (FC) magnetization was measured vs. decreasing temperature in constant field. Fig. 2 shows data for 0.1 T applied field. The high-temperature behavior was fit to a Curie-Weiss law, $\chi = \frac{C}{T - \Theta} + \chi_{dia}$, where $\chi_{dia}$ denotes a diamagnetic background. The value $C = 5.6 \times 10^{-5}$ K m$^3$/kg indicates an effective moment $p_{eff} = 5.5 \mu_B$ per Fe, close to the free-ion value, 5.9 $\mu_B$, for high-spin Fe ($p_{eff} = g[J(J+1)]^{1/2}$). $T_c$ obtained from the fit is $180$ K. The diamagnetic term, $\chi_{dia} = -8.2 \times 10^{-8}$ m$^3$/kg, is large and may be an overestimation due to rounding of the transition. Some distribution of $T_c$ seems likely because of the observed Fe concentration distribution. However, low temperature magnetization measurements agree with the Curie fit; $T_c = 170$ K is estimated from a modified Arrott plot (inset to Fig. 3).

A divergence of $\chi_{FC}$ and $\chi_{ZFC}$ starts near $170$ K, and becomes much more pronounced below $110$ K (Fig. 2). The remanence was also measured, warming the sample after removal of the field, and found to decrease with temperature, and vanish near $110$ K. The magnetization at 2 K (Fig. 2) is polarized to 0.75 $\mu_B$ per Fe in a small field. However, full saturation is not reached even at 7 T, where the magnetization corresponds to 1 $\mu_B$ per Fe. This value is considerably lower than expected, given the value $p_{eff} = 5.5 \mu_B$ obtained from the Curie fit. This suggests a canted or noncollinear spin configuration.

The observed magnetic behavior cannot be due to the small amount of FeGe$_2$, which has a spiral spin structure below 289 K, becoming commensurate at 263 K. These do not correspond to the observed transitions, and the observed moments clearly could not result from inclusions of this phase at the few percent level.

To further understand the magnetic behavior, in-phase ($\chi'$) and out-of-phase ($\chi''$) ac susceptibilities were measured under a 0.6 mT ac field, with the results shown in Fig. 4. The higher-temperature data could be fit to a Curie law with $T_c = 180$ K, in accord with the dc results. $\chi'$ exhibits a strong rise below 200 K, corresponding to the ferromagnetic transition. However, below a maximum, $\chi'$ decreases at lower temperatures and becomes frequency-dependent, while $\chi''$ also becomes frequency-dependent. The frequency dependence, combined with the decrease of ZFC vs. FC magnetization below 110 K, are characteristic of reentrant spin glass systems. We conclude that the transition near 170 K is ferromagnetic, while the 110 K irreversibility point corresponds to a spin glass freezing transition.

Frequency dependent $\chi_{AC}$ is found in spin glasses, while for ordinary ferromagnets the time-scale is much
too small, even for the critical slowing down region near $T_c$.\textsuperscript{15,16} Canted ferromagnets with a low-temperature anti-ferromagnetism have exhibited ac behavior similar to that of a reentrant spin glass\textsuperscript{23} however $\chi''$ in that case shows only an increase with frequency, and no shift in canting transition temperature. The variation of $\chi''$ peak position, $T_p$, per decade of frequency, $[dT_p/(\log f)/T_p]$, is 0.042 for Ba$_6$Ge$_{22}$Fe$_3$, which is in the range of values observed for spin glasses, 0.004 to 0.08.\textsuperscript{24}

Spin-glass reentrance is attributed to the freezing of transverse degrees of freedom in a ferromagnet containing disorder.\textsuperscript{15,16} Alternatively, a cluster-glass mechanism has been argued\textsuperscript{18} and it is clear that ferromagnetic clusters and considerable disorder in the ferromagnetic state\textsuperscript{23} do play a role in real materials. However, a cluster glass alone does not explain the present data, particularly the low-temperature saturation. A remanence increase on cooling in the glassy state is also typical of such spin glasses.\textsuperscript{18}

Fe occupancy of framework sites is below the percolation threshold, even for second-neighbor bonds, so it is likely that the mechanism for magnetic ordering is conduction-electron mediation, as in diluted magnetic semiconductors. For comparison, in (Ga$_{1-z}$Mn$_z$)As, Mn carries about 5 $\mu_B$, and $T_c$ scales linearly with small values of $x$, reaching $T_c = 110$ K for $x = 0.05$.\textsuperscript{19} The present system is quite similar in $T_c$ vs. $x$. Band-structure calculations\textsuperscript{22} indicate a gap below the Fermi level in Ba$_6$Ge$_{25}$ which may quite possibly be the $E_F$ location in the Zintl composition Ba$_6$Ge$_{24}$. The Zintl concept\textsuperscript{22} involves valence counting to give a closed-shell bonding configuration. Assuming valence 3 for Fe, Ba$_6$Ge$_{21.4}$Fe$_3$ is also a Zintl phase, and very close to the average composition found here. Thus it seems likely that $E_F$ is near a band edge in this material, and the semiconductor model is appropriate.

There is considerable interest in the effects of disorder on the magnetic behavior of magnetic semiconductors.\textsuperscript{24,25,26} The conduction-electron mediated interaction provides frustration, giving a non-collinear ordered state.\textsuperscript{23} For the case of (Ga$_{1-x}$Mn$_x$)N, the ground state appears to be a spin glass with no ferromagnetism.\textsuperscript{27} Here we observe a ferromagnetic transition and spin-glass state in the same material.

In summary, a Ba$_6$Ge$_{22}$Fe$_3$ clathrate was synthesized, exhibiting a ferromagnetic $T_c = 170$ K. Below 110 K, a transition to a reentrant spin glass was evidenced by the onset of frequency-dependent ac susceptibility and a characteristic field-dependent magnetization.

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