Silicon Clathrate with an *f*-Electron System

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A novel crystal of $Ba_6Ce_2Au_4Si_{42}$ with Ba and Ce encapsulated into silicon-polyhedral clusters is self-assembled from the state of elemental mixture. Each atom in the crystal is arranged in its well-defined position with a nanoscale period, causing unique interactions between the conduction and the magnetic electrons originating from the independent sources of Ba and Ce, respectively. In this system, the long-distant magnetic f electrons can interact with each other through nanoscale spacing with isotropic three dimensionality, leading to the occurrence of a unique spontaneous spin ordering at 6.5 K.

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New aspects in magnetism have arisen recently with the advent of nanomaterials. Nanocage structures directed to magnetism have become a very important issue, as seen in endohedral fullerenes [1] and in a series of rare-earth boron compounds [2,3]. Giant magnetoresistance in manganese copper oxides has also gained intense interest from the viewpoint of the unique interactions between magnetic and conduction electrons [4,5]. We have made a new approach to designing a novel magnetic material on a basis of silicon nanocluster crystals with polyhedral cage structure, where an f-block element Ce and alkaline-earth metal Ba encapsulated inside the cluster cage act as independent sources of magnetic and conduction electrons. Since both of the new aspects in magnetism described above can be realized with nanoscale control in position of the elements, silicon clathrates with magnetic elements will provide a good scientific stage for shedding a new light on magnetism in nanoscale.

Silicon nanoclusters, Si_{20}, Si_{24}, and Si_{28}, were first evidenced by Kasper *et al.* in nanocage structured materials, so-called clathrates [6]. Silicon clathrates are classified into two types: typically Si_{46} (type I) and Si_{136} (type II) with cubic lattice, in which the silicon atoms are tetrahedrally (sp^3) bonded like a diamond phase of silicon [6–8]. The type I clathrate studied here consists of dodecahedral Si_{20} cages with six interstitial 6*c* positions linking these cages thus automatically forming tetrakaidecahedral cages, as seen in Fig. 1. These cages generally encapsulate alkali metals such as Na, K, and Rb to stabilize the clathrate structure. Recently, the introduction of Ba atom into these cages has been found to be essential for the occurrence of superconductivity [9,10]. Band calculations of $Na_2Ba_6Si_{46}$ have suggested that the Ba 5*d* orbitals are strongly hybridized with the Si_{46} conduction band, giving very high density of states at the Fermi level [11,12]. This indicates that the electronic properties of silicon clathrates can greatly be modified by the element inside the cage having electrons near the 5*d* level.

We have focused on Ce as an inclusion element since the 4f electrons of Ce are considered to be in a less bound state between magnetic and metallic states and are expected to strongly hybridize with conduction electrons spreading over the silicon network [13]. In this paper, a new system of $Ba_6Ce_2Au_4Si_{42}$ is presented, where the interactions between magnetic f and conduction electrons play an important role for spin ordering.

The clathrate $Ba_6Ce_2Au_4Si_{42}$, as seen in Fig. 1, was made by simply melting the stoichiometric amounts of the elements using a rf-induction furnace under an argon

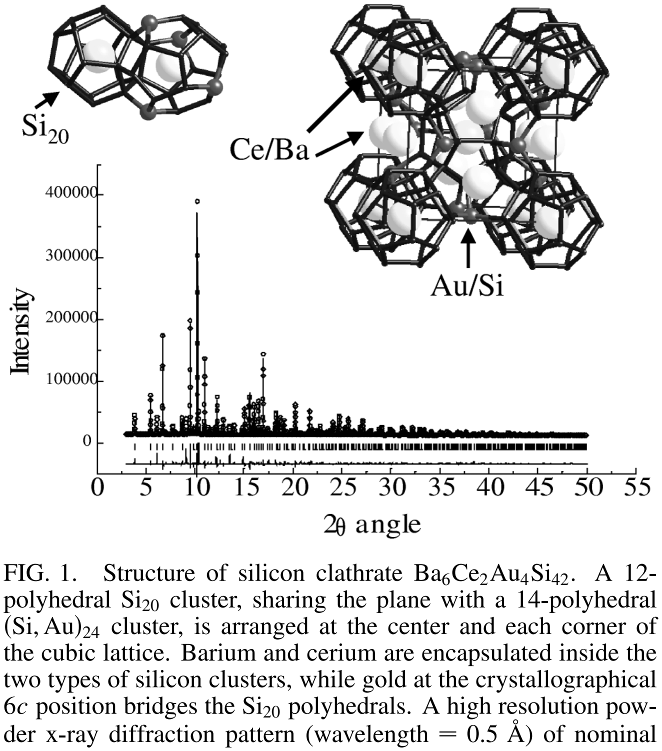

FIG. 1. Structure of silicon clathrate $Ba_6Ce_2Au_4Si_{42}$. A 12-polyhedral Si_{20} cluster, sharing the plane with a 14-polyhedral $(Si,Au)_{24}$ cluster, is arranged at the center and each corner of the cubic lattice. Barium and cerium are encapsulated inside the two types of silicon clusters, while gold at the crystallographical 6*c* position bridges the Si_{20} polyhedrals. A high resolution powder x-ray diffraction pattern (wavelength = 0.5 Å) of nominal stoichiometry $Ba_6Ce_2Au_4Si_{42}$ is shown together with Rietveld refinement.

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atmosphere. It should be noted that the silicon atoms are self-assembled into the clathrate structure during the process of natural cooling from the melt with the gold atoms acting to promote the assembly. However, it is crucial for the clathrate formation that the number of Au introduced is in the vicinity of four. This observation is in contrast to the situation encountered in producing typical clathrates, where the type I structure is stabilized with as much as Au up to six stoichiometries [14]. The product thus obtained was analyzed by x-ray diffraction measurements from room temperature down to 9.0 K using synchrotron radiation at SPring-8 (beamline BL02B2) and KEK (PF-BL1B).

Preliminary Rietveld refinement using a CERIUS2 program has been performed assuming that two Ce and six Ba atoms are spherically encapsulated inside the dodecahedral (Si_{20}) and tetrakaidecahedral cages (at the $2a$ and $6d$ positions) and four Au and two Si atoms are at the $6c$ positions in a random fashion, resulting in a reasonable R_{wp} factor of 7.0%. The lattice parameter of $Ba_6Ce_2Au_4Si_{42}$ at room temperature is 10.42 Å with a space group of $Pm\bar{3}n$. This is the first compound that encapsulates an f-electron element inside the silicon cluster cage. Because of the encapsulation of Ba and Ce, the compound is air stable like endohedrally doped C_{82}, while C_{60} fullerides are generally air sensitive.

Expecting new magnetic properties in $Ba_6Ce_2Au_4Si_{42}$, magnetization was measured under a low magnetic field. When temperature was decreased from 16 to 1.8 K under 20 G, a spontaneous magnetization was observed with steep increase at 6.5 K, as seen in Fig. 2. Hysteresis was also observed when the magnetic field was scanned in a loop of 3000 G at 1.8 K. These results show that a ferromagnetic transition occurs in this crystal. This is very much in contrast to the fact that $CeSi_2$, a well-known Ce-Si compound consisting of planar three-coordinated silicon, is paramagnetic [15]. It is surprising that such large coercive force (ca. 1400 G) as seen in the inset of Fig. 2 was observed in this dilute magnetic system (9 wt % of Ce).

Looking into the magnetization curve (Fig. 2) in detail, the shape of the curve observed is convexed upward, and this suggests that an antiferromagnetic spin ordering is also involved. We have, therefore, checked the evolution of magnetic moment per Ce atom as a function of magnetic field at 1.8, 4.4, and 10 K, as seen in Fig. 3. At 4.4 K just after the ferromagnetic transition, the magnetization increases steeply towards the saturation around 500 G although it still monotonously increases with magnetic field. On the other hand, at 1.8 K, the magnetization is first suppressed under low magnetic fields and then sharply increases around 1000 G to cross over the curve measured at 4.4 K, ending up with a continuous increase to a final value of about $0.8\mu_B$ (Bohr magneton) at 5×10^4 G. No specific change was observed for the M-B curve measured above the ferromagnetic transition temperature. These M-B curves can rationally be explained in terms of the spin flops from an antiferromagnetic to a ferromagnetic state in the feasible magnetic alignment direction, and therefore certainly shows the existence of antiferromagnetic ordering at low temperatures. The Weiss temperature of -25 K obtained from the Curie-Weiss analysis also supports an antiferromagnetic interaction competing at lower temperatures.

It is interesting to note that the magnetic moment per Ce atom of 0.8 μ_B estimated earlier is obviously smaller than that estimated from the Curie-Weiss plot between 45 and 300 K at 10^4 G. The effective moment from isolated electron spins in this temperature range is calculated to be ca. $2.7\mu_B$ per Ce atom, which is close to the L-S coupling J value $(5/2)$ of Ce^{3+} ion. This seems to indicate either that the f electrons of Ce begin to itinerate through scattering with conduction electrons or that an antiferromagnetic

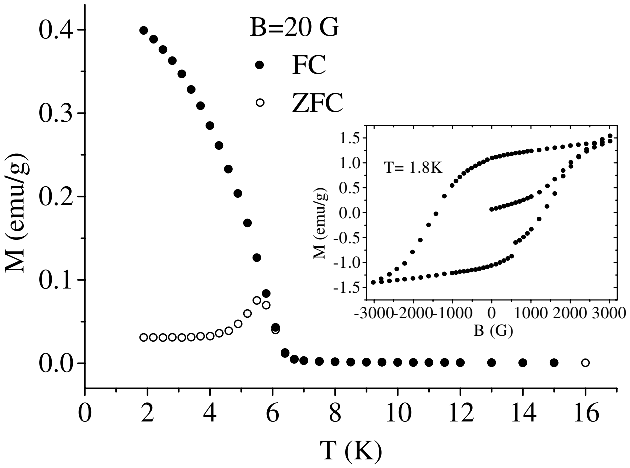

FIG. 2. Temperature dependence of magnetization measured in zero-field cooling (open circles) and field cooling (closed circles) under an applied magnetic field of 20 G. The inset shows a hysteresis at 1.8 K measured with a 3000 G loop.

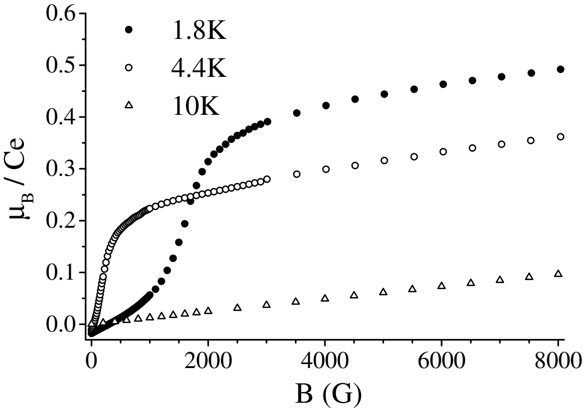

FIG. 3. Evolution of magnetic moment per Ce atom with unit of Bohr magneton as a function of magnetic field, measured at 1.8 K (closed circles), 4.4 K (open circles), and 10 K (open triangles).

spin cant state is generated at low temperatures. Furthermore, it may also be worthwhile to note that the continuous increase in the *M-B* curve has a very large gradient of the order of 10^{-2} emu G^{-1} mol^{-1} at low temperatures, suggesting the influence of f electrons with a heavy-fermion behavior.

A magnetization curve was also measured in another mode. First, the temperature was set at 1.8 K under zero field within experimental errors of our SQUID apparatus and magnetization was monitored under 20 G with increasing temperature to 16 K. Interestingly, the curve observed in this zero-field cooling mode showed a quite different temperature dependence from that in the field cooling mode. This is very unusual for conventional ferromagnetic interactions. One may assume that a spin glass state will occur due to the shift of the Ce atom from the center of the cage causing a disorder in periodicity or in symmetry of the crystal [16]. However, high resolution x-ray diffraction patterns at low temperatures down to 9 K did not show any such symptom in our experiments. Even if a slight displacement of Ba and Ce atoms occurs, direct spin-spin pairing may not be serious as is observed in Gd@C_{82} [17]. To the best of our knowledge, a similar phenomenon has been reported only for a few compounds, like TDAE-C_{60} [18] and a MnTTP derivative [19], which have still actively been debated to date.

Although it is difficult to satisfactorily elucidate the mechanism of the ferromagnetic and the antiferromagnetic interactions as well as the other unusual magnetic behaviors at the moment, it would at least be worthwhile to discuss here. One of the most important factors responsible for the occurrence of the magnetic orderings would be the increase in the density of states at the Fermi level $N(E_F)$ associated with itinerant f electrons of Ce as well as conduction electrons from Ba. Actually, when Ce is replaced by La, no significant magnetization is observed in $Ba_6La_2Au_4Si_{40}$, supporting that the $4f$ electrons on Ce atoms are involved in the magnetic phenomena observed at low temperatures. Considering the large interval between Ce atoms (8.3 Å on the average), it is plausible to suppose here that the spin ordering of the f electrons can result from their RKKY-type interactions via the conduction electrons spreading over the silicon network.

As seen in the general formula of spin polarization of conduction electrons in RKKY mechanism $\sigma(r) \propto \frac{N_{E_F}\cos(2k_F r)}{r^3} S_Z$ [20], $N(E_F)$ is a very important factor for electron spin ordering, where $N(E_F)$ is proportional to $m^* \rho^{1/3}$ (m^*: effective mass, ρ: carrier concentration). Therefore, experiments to see how the magnetic ordering is affected by $N(E_F)$ is crucial for confirming the involvement of the RKKY type mechanism. Although such experiments are generally difficult in the conventional materials, it would be possible in this system since the introduction of Au atoms are known to decrease $N(E_F)$ in silicon clathrates [13]. These Au atoms with large electron affinity will function to decrease the value of ρ. When ρ decreases, interactions between f and conduction electrons would be weakened and then m^* will also decrease. Actually, when slightly more stoichiometric amounts of Au are incorporated into the system, a sharp decrease in ferromagnetization is observed at low temperatures while the magnetic moment per Ce atom is recovered to become large, showing that the magnetic ordering in this system is very sensitive to $N(E_F)$. This is consistent with our thought that RKKY type mechanism is of importance for the spontaneous spin ordering.

The spin polarization of conduction electrons is generally independent of temperature since E_F is greater than $k_B T$ in the conventional materials. However, when m^* is large and ρ is small so that E_F can be smaller than $k_B T$, as seen in a heavy fermion system, the spin polarization formula then becomes temperature dependent and is represented by $\sigma(r) \propto m^{*2} T \frac{\exp\{-(\pi k_B T/E_F) k_F r\}}{r^2} S_Z$. If one tentatively assumes that the ferromagnetic transition occurs when r becomes the half of the interval between Ce^{3+} ions (4.1 Å), m^* is deduced to be ca. $350m$ (m: free electron mass) at 6.5 K from the equation of $r = E_F/(\pi k_B k_F T) = \hbar^2 (3\pi^2 \rho)^{1/3}/(2m^* \pi k_B T)$, indicating a strong correlation among electrons. According to the framework of the free-electron model, m^* can also be calculated from the value of $N(E_F)$ which is equivalent to spin susceptibility (χ_{Pauli}). We have determined χ_{Pauli} from the gradient of the *M-B* curve in the linear portion with corrections for Curie and core-diamagnetic susceptibilities using a method similar to the literature [13]. The value of χ_{Pauli} at 300 K was found to be 6.5×10^{-7} emu G^{-1} g^{-1}, being equivalent to $m^* = 3m$. The same analysis at 10 and 1.8 K has given $\chi_{\mathrm{Pauli}} = 3.0 \times 10^{-5}$ and 1.3×10^{-5} emu G^{-1} g^{-1}, being equivalent to $m^* = 140m$ and $56m$, respectively. Although the free-electron model is simple for understanding of this system, it seems to describe the way f electrons itinerate with heavy fermion behavior as temperature decreases.

In general, f electrons are rarely involved in the electronic properties since their energy levels are deeply away from the Fermi level. However, once they are involved, the electronic properties would artificially be controlled. Since silicon clathrates have a great capacity for accommodating a variety of transition metals such as Au, Ag, and Cu [8], the strength of interactions among the f and the conduction electrons could be controlled over a wide range. Considering the situation that $Na_2Ba_6Si_{46}$ and Ba_8Si_{46} are superconductors [9,10], it is curious to search for the occurrence of superconductivity also in this system, as seen in the first f electron superconductor $CeCu_2Si_2$ [21]. It is interesting to see whether the transition into the superconducting state could be controlled by pressure, as seen in certain antiferromagnetic compounds [22].

Finally, when compared to the d-electron systems reported for perovskite $La_{1-x}Sr_xMnO_3$ [4,5] and pyrochlore $Tl_2Mn_2O_7$ [23], the present f-electron system would be quite different in terms of the effect of crystal field because Ce atoms are encapsulated inside the polyhedral Si cages. In addition, the double exchange mechanism important in such Mn d-electron systems will be less important in this system. This paper clearly demonstrated that a new system has been created with unique magnetic properties. Essential to learning more in the future will be the nature of the electronic band of this system and the real mechanism in the long-ranged spin ordering observed.

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