GERMANIUM CLATHRATE WITH *d*-TRANSITION ELEMENT

New aspects in magnetism have recently arisen with the advent of nano-materials. Nano-cage materials directed to magnetism have become one of the most important issues in materials science, as seen in endohedral-fullerenes [1] and in a series of rare-earth boron compounds [2,3]. Giant magneto-resistance in manganese copper-oxides has also gained intense interests from the scientific and technological fields which concentrates on the unique interactions between magnetic- and conduction-electrons [4,5].

In this system, the long-distant magnetic *d*-electrons can interact with each other through nano-scale spacing in an isotropic three-dimensionality, leading to the occurrence of a unique spontaneous spin-ordering at 10 K.

The clathrate $Ba_8Mn_2Ge_{44}$, was made by simply melting the stoichiometric amounts of the elements using an RF-induction furnace under an argon atmosphere. It should be noted that the germanium atoms are melt followed by self-assembling into the clathrate structure during the process of natural

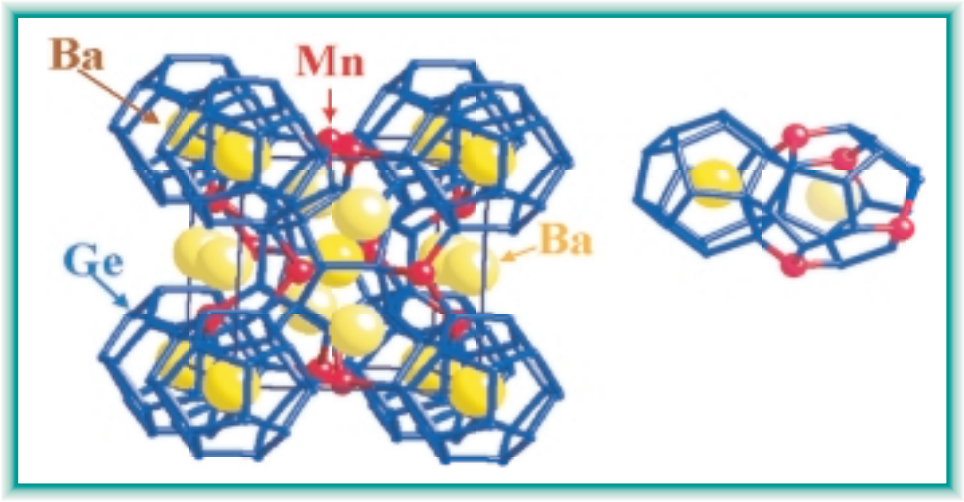


Fig. 1. Structure of Ge_{46} Clathrates endohedrally encapsulating Ba and magnetic d-electron Mn.

We have taken a new approach in designing a novel magnetic material on a model of germanium nano-cluster crystals with a polyhedral cage structure [6], where *d*-block element Mn resides on the position connecting Ge_{20} dodecahedra cluster cages and alkaline-earth metals Ba are encapsulated inside the cluster cages as shown in Fig. 1 [7]. The both elements thus introduced act as independent sources of magnetic- and conduction- electrons.

cooling. The product obtained was then analyzed by X-ray diffraction measurements at room temperature using synchrotron radiation at beamline **BL02B2** as shown in Fig. 2.

Preliminary Rietveld refinement using a Cerius [2] program has been performed, assuming that two Mn atoms reside on the crystallographic *6c* positions and eight Ba atoms are spherically encapsulated both inside the dodecahedral Ge_{20}

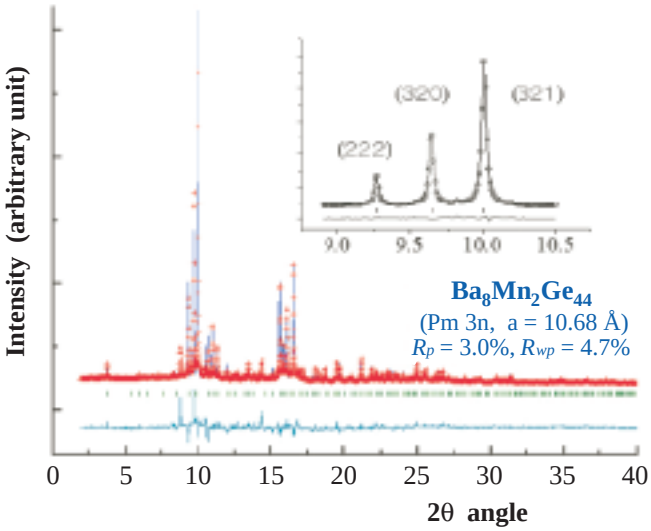


Fig. 2. High resolution X-ray diffraction spectrum of $Ba_8Mn_2Ge_{44}$.

and tetrakaidecahedral Ge_{24} cages (at the *2a* and *6b* positions). This resulted in a reasonable R_{wp} factor of 4.7%. The lattice parameter of $Ba_8Mn_2Ge_{44}$ at room temperature is 10.68 Å with a space group of Pm-3n. This is the first compound that accommodates *d*-electron element Mn in germanium type I clathrates. Since Ba is encapsulated, the compound is air-stable like endohedrally-doped C_{82}, being compared to the fact that C_{60} fullerides are generally air-sensitive.

Expecting new magnetic properties in $Ba_8Mn_2Ge_{44}$, we measured the magnetization under a low magnetic field. When the temperature was decreased from 20 K to 1.8 K under 10 G, a spontaneous magnetization was observed with a steep increase in intensity at 10 K, as seen in Fig. 3. A hysteresis was also observed when the magnetic field was scanned in a loop of 100 G at 1.8 K. These results demonstrate that a ferromagnetic transition occurs in this crystal. It should be emphasized that the observation of the ferromagnetic behavior is not due to the conventional magnetic direct-interactions. It is unambiguous that the ferromagnetic ordering occurs in this dilute magnetic system (9 wt% of Mn), since a hysteresis was seen as shown in the inset of Fig. 3 even though the value is small.

We have also used another mode to investigate magnetic behavior. First, the temperature was set at 1.8 K under a zero-field within the experimental errors of our SQUID apparatus, and magnetization was monitored under 10 G with increasing temperature to 16 K. Interestingly, the curve observed in this zero-field cooling mode (ZFC) showed a small different temperature dependence from that in the field cooling mode (FC). This is quite unusual for conventional ferromagnetic interactions.

Although it still needs the further investigation to have a satisfactory elucidation about the mechanism of the magnetism in this compound, it would at least be worthwhile to discuss here. One of the most important factors responsible for the occurrence of the magnetic orderings is likely the increase in the density of states at the Fermi level $N(E_F)$ associated with conduction electrons from Ba as well as a little itineration of *s,d*-electrons on Mn. In fact, when Mn is replaced by another nonmagnetic element like Au, no significant magnetization was

observed in $Ba_8Au_6Ge_{40}$, supporting the idea that the *d*-electrons on Mn atoms are essentially involved in the magnetic phenomena observed at low temperatures. Considering the large average interval of 8.3 Å between Mn atoms, it is plausible to suppose here that the spin ordering of the *d*-electrons can result from their RKKY like interactions via the conduction electrons spreading over the clathrate network.

Since the new aspects in magnetism described in the present paper can be realized with nano-scale control in the position of the elements, clathrates with magnetic elements will provide a good scientific stage for shedding a new light on magnetism in nano scale.

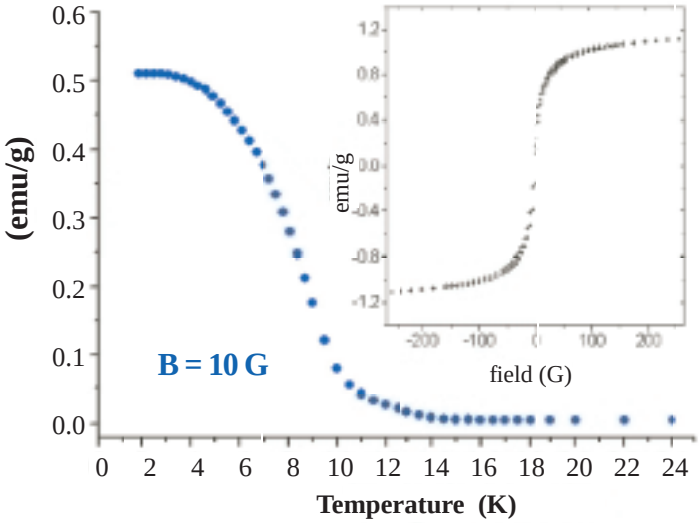
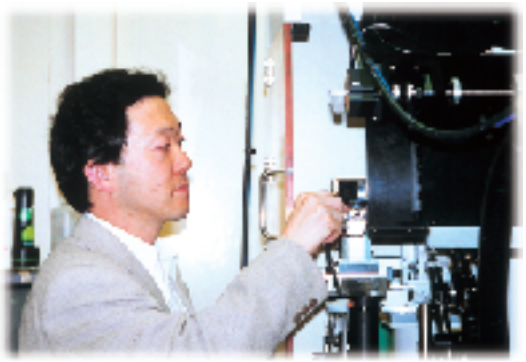


Fig. 3. Spontaneous magnetization curve of $Ba_8Mn_2Ge_{44}$ measured under 10 G.

Katsumi Tanigaki[a,b], Tetsuji Kawaguchi[a] and Masahiro Yasukawa[c]

(a) Osaka City University
(b) PRESTO, Japan Science and Technology Corp.
(c) CREST, Japan Science and Technology Corp.

E-mail: tanigaki@sci.osaka-cu.ac.jp



References

[1] T. Ogawa *et al.*, J. Am. Chem. Soc. **122** (2000) 3538.
[2] T. Susaki *et al.*, Phys. Rev. Lett. **82** (1999) 992.
[3] D.P. Young *et al.*, Nature **397** (1999) 412.
[4] S. Jin *et al.*, Science **264** (1994) 413.
[5] Y. Tokura *et al.*, J. Phys. Soc. Jpn. **63** (1994) 3931.
[6] H. Kawaji *et al.*, Phys. Rev. Lett. **74** (1995) 1427.
[7] R.F.W. Herrmann, K. Tanigaki, T. Kawaguchi, S. Kuroshima and O. Zhou, Phys. Rev. B **60** (1999) 13245; T. Kawaguchi, K. Tanigaki and M. Yasukawa, Appl. Phys. Lett. **77** (2000) 3438.