EXOTIC MAGNETIC AND ELECTRICAL BEHAVIORS IN THE PHASE SEPARATED STATE OF THE NATURALLY NANO-LAYERED $R_5(Si,Ge)_4$ INTERMETALLICS, WHERE R IS A HEAVY LANTHANIDE ELEMENT

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Introduction

The $R_5(Si,Ge)_4$ compounds, where R is a rare earth element, crystallize in a unique series of 3 very closely related structures in which identical nano-layers are stacked above one another, with pairs of (Si,Ge) atoms binding the layers together, see Fig. 1. In the orthorhombic Gd_5Si_4-type structure (O-I) the layers are held together by Si-pairs of atoms which are ~2.6 Å apart, i.e. "strongly bonded" (structure A in Fig. 1). In the orthorhombic Sm_5Ge_4-type structure (O-II) the layers are held together by Ge-pairs of atoms which are ~3.5 Å apart, i.e. "weakly bonded" (structure C in Fig. 1). The third member of this group is a hybrid of O(I) and O(II) and has the monoclinic $Gd_5(Si_2Ge_2)$-type structure (M), in which pairs of the nano-layers are held together by the strongly bonded (Si,Ge pairs), while the neighboring pairs of nano-layers are held together by the weakly bonded (Si,Ge) pairs (structure B in Fig. 1) [1,2].

In the $Gd_5(Si,Ge)_4$ system O-I is always ferromagnetic (FM) below T_C while O-II orders antiferromagnetically (AFM) and M is always paramagnetic (PM). M and O-II transform to the FM O-I phase when cooled or under an applied magnetic – a reversible first order coupled magnetostructural transformation and results in a giant magnetocaloric effect (GMCE), a giant magneto-resistance (GMR) and a colossal magnetostriction (CMS) [1].

Heavy Lanthanide $R_5(Si,Ge)_4$ Compounds

For the $R_5(Si,Ge)_4$ compounds, when R is a non-Gd heavy lanthanide (i.e. Tb, Dy, Ho, or Er) the electrical and magnetic behaviors are quite different from those of the $Gd_5(Si,Ge)_4$ series, because of their strong magnetocrystalline anisotropies. Although the same crystal structures are observed in the $R_5(Si,Ge)_4$ phases the crystallographic M→O(I), or O(II)→O(I) transformations do not go to completion. As a result, the two phases co-exist forming a crystallographic phase separated state over a wide range of temperatures and magnetic fields. The existence of these phase separated states in the $R_5(Si,Ge)_4$ compounds leads to some unusual electrical and magnetic phenomena.

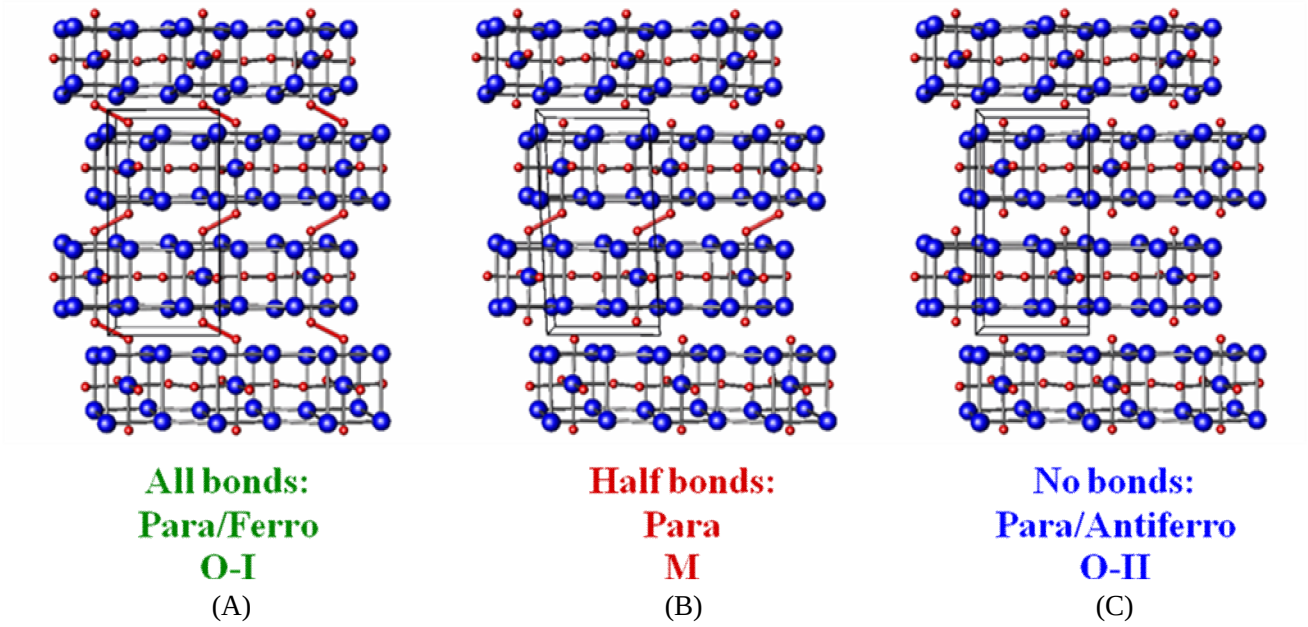

Fig. 1 (Color online) The three $R_5(Si,Ge)_4$ crystal structures: (A) the orthorhombic Gd_5Si_4-type, (B) the monoclinic $Gd_5Si_2Ge_2$-type, and (C) the orthorhombic Sm_5Ge_4-type. The large (blue) spheres are the R metals and the small (red) spheres are the (Si,Ge) atoms. The solid (red) line connecting the (Si,Ge) pairs between the layers indicates they are strongly bonded (~2.6 Å separation). The absence of this line indicates they are weakly bonded (Si,Ge) pairs (~3.5 Å separation).

In $Tb_5Si_{2.2}Ge_{1.8}$ the magnetoresistance (MR) at ~120 K along the three principal crystallographic axes is very anisotropic. It varies from zero along the *b*-axis to -15% along *c* to an incredible colossal MR of +200% in *a*, see Fig. 2 [3]. This effect is due to the geometry of the interphase boundaries between the low temperature majority phase, O(I) and the minority phase, M. In the *b* and *c* directions the adjacent crystallite boundaries of the O(I) and M phases are coherent and little or no scattering of the conduction electrons occurs as the electrons travel through the boundary of neighboring M and O(I) crystallites (the crystallites are 5 to 20 mm in size). However, along the *a*-direction the boundary of the M phase is skewed by the non-90° monoclinic angle relative to the adjacent orthorhombic crystallite giving rise to incoherency and a large scattering cross section as the $Tb_5Si_{2.2}Ge_{1.8}$ phase goes through the M ↔ O(I) phase transition.

In Dy_5Si_3Ge we have a different and again a remarkable magnetic phenomenon due to the phase separated state. In this material the M phase is magnetically soft and the O(I) phase is a hard magnet. As the system cools below the Curie point of 54 K, the M phase begins to transform to the O(I) phase, but only 47% of the Dy_5Si_3Ge alloy transforms to the O(I) phase [6]. In this phase separated state the M and O(I) are intimately mixed and exchange-coupling between the neighboring soft and hard magnetic phase occurs lead to a spring magnet behavior. The B vs. H curves exhibit a nearly ideal rectangular hysteresis loops below 10 K, and at 2 K the energy product is double that of $Nd_2Fe_{14}B$ at 298 K, see Fig. 3 [4].

Conclusion

In addition to the GMCE, GMR, and CMS behaviors observed in $Gd_5(Si,Ge)_4$, we have observed other amazing extremum behaviors for R = Tb and Dy. For $Tb_5Si_{2.2}Ge_{1.8}$ the MR goes from 0 to +200% by rotating the crystal 90°. In Dy_5Si_3Ge we found the first ever, nature-designed, exchange-coupled permanent magnet which has an energy product twice as large as ever observed.

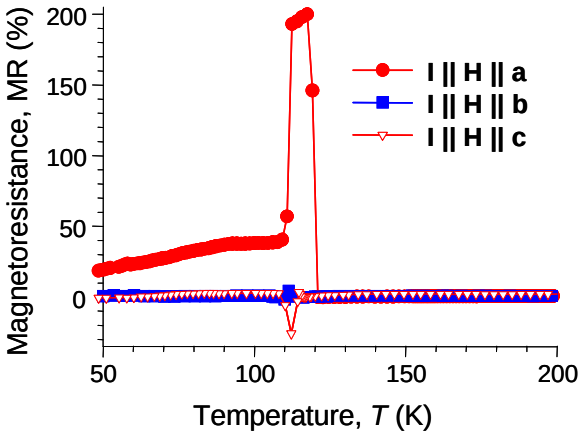

Fig. 2 (Color online) Temperature (*T*) dependence of the magnetoresistance of single crystal $Tb_5Si_{2.2}Ge_{1.8}$.

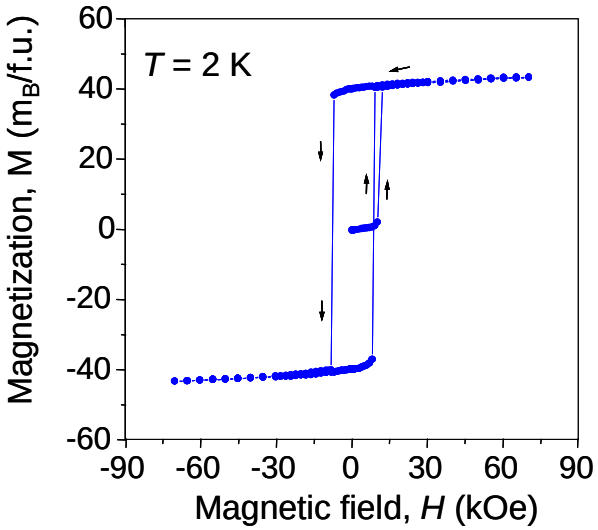

Fig. 3. (Color online) Magnetization isotherm of Dy_5Si_3Ge at 2 K in applied fields up to 70 kOe.

Acknowledgement

This work was supported by the Office of Basic Energy Sciences of the Office of Sciences of the U.S. Department of Energy under Contract No. DE-AC02-07CH11358 with Iowa State University of Science and Technology.

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