Structural And Magnetic Properties Of RFe_6Ge_6 (R=Y, Gd, Tb, Er)

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Abstract—**A series of RFe_6Ge_6 (R=Y, Gd, Tb, Er) compounds have been prepared by arc-melting. Structural studies using x-ray diffraction (XRD) show that all four as-cast alloys belong to the hexagonal P6/mmm space group with similar lattice parameters (for YFe_6Ge_6, a = 5.12Å and c = 4.07Å). After annealing at 900°C for two weeks, both YFe_6Ge_6 and $TbFe_6Ge_6$ transform into the orthorhombic Cmcm structure. Mössbauer spectroscopy and magnetisation measurements show that all of the alloys are antiferromagnetically ordered at room temperature. We find a single Fe crystallographic site, consistent with the RFe_6Ge_6 structures. Both the room temperature ^{57}Fe hyperfine field and the Néel temperature (T_N) are largely independent of the rare-earth, being 14.9(1) T and 487 K respectively for YFe_6Ge_6.**

I. Introduction

The crystallographic and magnetic properties of rare-earth intermetallic compounds of the form RFe_6Ge_6 (R = Sc, Y, rare-earths (Gd–Lu)) were recently reported by Venturini *et al.* [1]. Such 1-6-6 compounds form in a variety of closely related structures [2], [3] and it was claimed that the 1-6-6 structure type found in the RFe_6Ge_6 series changes with increasing R atomic radius as $HfFe_6Ge_6$ (P6/mmm) (R=Sc,Lu) → $HoFe_6Sn_6$ (Immm) (R=Tm,Er) → $TbFe_6Sn_6$ (Cmcm) (R=Ho,Y,Dy,Tb). Interestingly, the structure of $GdFe_6Ge_6$ was indexed in terms of a new structural variant (space group Pnma) with unusually large a and c lattice parameters (a = 61.43Å, b = 8.137Å and c = 79.79Å). A similar structural variation had been reported previously in the RFe_6Sn_6 series [3] although the suggested occurrence of no less than six different structural variants for a rare-earth atomic size variation of less than 2% is somewhat surprising. The various 1-6-6 structures are derived from different stacking sequences of two fundamental building blocks: the hexagonal $HfFe_6Ge_6$ (space group P6/mmm) block and the orthorhombic $ScFe_6Ga_6$ (space group Immm). $HfFe_6Ge_6$ is an ordered, filled derivative of the binary B35-type structure of FeGe and FeSn [4] while $ScFe_6Ga_6$ is a derivative of the tetragonal $ThMn_{12}$ (space group I4/mmm) structure [5]. Denoting these two building blocks as H and S, respectively, the observed structures in the RFe_6Ge_6 series result from the following stacking arrangements: $HfFe_6Ge_6$ HH, $HoFe_6Sn_6$ HSHHSH and $TbFe_6Sn_6$ HSHSH.

In this paper we present the results of a structural and magnetic study of the RFe_6Ge_6 compounds (R=Y,Gd,Er and Tb). We find that all as-cast samples have the same crystallographic structure namely YCo_6Ge_6 (P6/mmm – a partially disordered form of the $HfFe_6Ge_6$ structure). Upon annealing, the structures of YFe_6Ge_6 and $TbFe_6Ge_6$ change to the orthorhombic $TbFe_6Sn_6$(Cmcm) structure while $GdFe_6Ge_6$ and $ErFe_6Ge_6$ remain in the YCo_6Ge_6 structure. As earlier magnetic studies have concentrated on macroscopic properties, we use ^{57}Fe Mössbauer spectroscopy here to investigate the microscopic magnetic properties of these alloys, and relate them to the structural changes observed.

II. Experimental Methods

The compounds were synthesized from stoichiometric amounts of the commercially available high-purity elements: Fe (99.98%), Y (99.99%), Gd (99.9%), Tb (99.99%), Er (99.9%) and Ge (99.999%). The rare-earth elements were pre-melted in an arc furnace under a Ti-gettered argon atmosphere. As-cast samples were prepared by arc-melting and each sample was turned and re-melted several times to homogenize the sample. For annealing, each sample was sealed in a quartz tube under a partial pressure of Helium and annealed at 900°C for two weeks, followed by quenching in water.

Powder x-ray diffraction (XRD) patterns were obtained using Cu-K_α radiation on an automated Nicolet-Stoe diffractometer. For the purposes of indexation, the experimental XRD patterns were compared with theoretical patterns generated using the LAZY-PULVERIX [6] program. Thermogravimetric analysis was carried out on a Perkin-Elmer TGA-7 system in a small field gradient. Mössbauer spectra were obtained in standard transmission geometry with a ^{57}Co*Rh* source. The spectra were calibrated against a natural α-Fe foil. Néel

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temperatures (T_N) were determined using zero-velocity Mössbauer thermal scans, carried out in a furnace containing ~0.2 atm. of pre-purified Argon and operating with a temperature stability of ±0.1K. Differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-2 was also used to measure T_N by observing the heat capacity signature of the transition. Magnetisation measurements were made on a conventional Vibrating sample magnetometer (VSM) in fields up to 1.5 Tesla.

III. Results and Discussion

In Fig. 1 we show the powder XRD patterns obtained on the as-cast and annealed YFe_6Ge_6 samples. The patterns obtained from all of the as-cast samples can be indexed according to the hexagonal P6/mmm space group, with some small peaks due to impurities of tetragonal RFe_2Ge_2 (space group I4/mmm). However on annealing, two of the alloys (YFe_6Ge_6 and $TbFe_6Ge_6$) no longer have the hexagonal P6/mmm structure although their new structure is closely related to P6/mmm. This may be inferred from the fact that the intense peaks of both patterns shown in Fig. 1 are similar although the annealed pattern exhibits weaker, additional peaks. Comparison of the patterns with theoretical patterns indicated that the structures of annealed YFe_6Ge_6 and $TbFe_6Ge_6$ belong to the orthorhombic Cmcm space group. The lattice parameters and structures deduced from the XRD patterns of the as-cast and annealed RFe_6Ge_6 samples are given in Table 1.

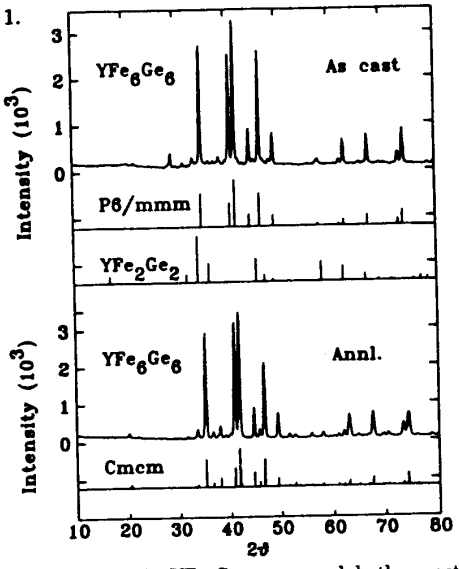

Fig. 1. XRD patterns for YFe_6Ge_6 compounds both as cast and annealed. Note that the as cast sample matches the P6/mmm pattern, while the annealed sample matches Cmcm.

Room temperature Mössbauer spectroscopy (Fig. 2) shows that all of the compounds are magnetically ordered with a single iron site which has a hyperfine field of 14.9 T in YFe_6Ge_6. The as-cast samples showed varying amounts of a non-magnetic phase, identified as tetragonal RFe_2Ge_2 both from the Mössbauer parameters and XRD results. Annealing at 900°C for two weeks greatly reduced the level of the contaminant phase, as can be seen in the lower spectrum in Fig. 2. VSM and TGA measurements show that the compounds exhibit no spontaneous magnetization, ruling out ferri- or ferro- magnetic spin configurations, and confirming that the alloys are antiferromagnetically ordered.

TABLE I

The structural configuration and lattice parameters of the RFe_6Ge_6 compounds. Note: there is a structural change on annealing for YFe_6Ge_6 and $TbFe_6Ge_6$.

Compound	State	a(Å)	b(Å)	c(Å)	Space group	Type
YFe_6Ge_6	As cast	5.128(9)	—	4.07(1)	P6/mmm	YCo_6Ge_6
	Ann.	8.12(1)	17.72(3)	5.103(6)	Cmcm	$TbFe_6Sn_6$
$GdFe_6Ge_6$	As cast	5.121(7)	—	4.05(1)	P6/mmm	YCo_6Ge_6
	Ann.	5.120(4)	—	4.075(6)	P6/mmm	YCo_6Ge_6
$TbFe_6Ge_6$	As cast	5.124(3)	—	4.062(3)	P6/mmm	YCo_6Ge_6
	Ann.	8.127(6)	17.67(4)	5.138(7)	Cmcm	$TbFe_6Sn_6$
$ErFe_6Ge_6$	As cast	5.110(3)	—	4.046(4)	P6/mmm	YCo_6Ge_6
	Ann.	5.107(2)	—	4.045(3)	P6/mmm	YCo_6Ge_6

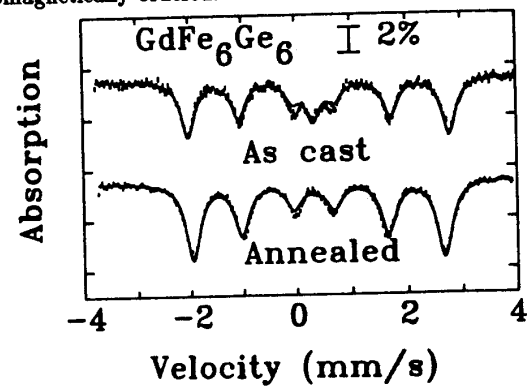

Fig. 2. Mössbauer spectra for $GdFe_6Ge_6$ compounds. The decrease in impurity level in the annealed sample is apparent.

Fig. 3 shows the room temperature hyperfine fields (B_{hf}) in all four of the RFe_6Ge_6 compounds studied here, in both the as cast state and after annealing. The observed field of ~15 T, is slightly less than half that found in α−Fe, and suggests an iron moment of about $1\mu_B$ in these alloys. The results also indicate that there is a weak dependence on the rare-earth present, with a steady decrease apparent across the series. Furthermore, the decrease in B_{hf} on annealing, which is also small, does not depend on whether the alloy changes structure, strongly suggesting that the two structures observed are closely related.

Several methods were used to obtain the ordering temperatures. Given the absence of a spontaneous magnetisation, the most direct method available was the temperature dependence of B_{hf} shown in Fig. 4 for YFe_6Ge_6.

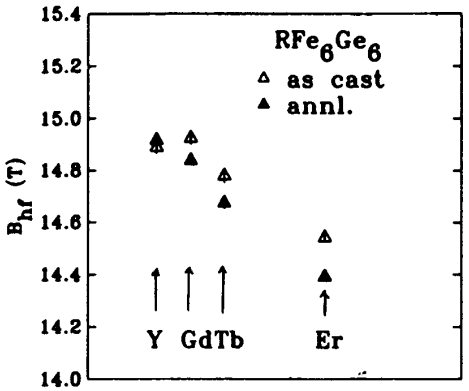

Fig. 3. The room temperature hyperfine fields (B_{hf}) of the as-cast and annealed RFe_6Ge_6 samples.

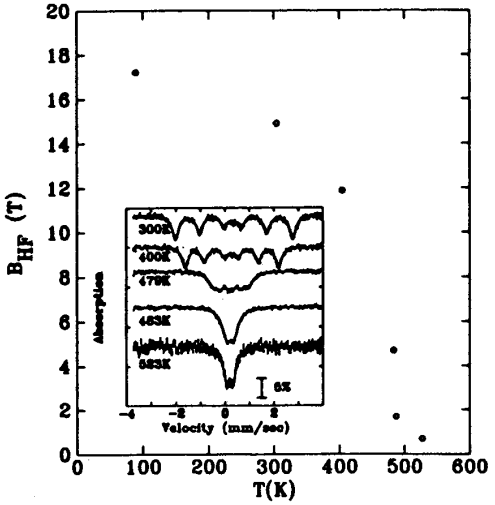

Fig. 4. Temperature dependence of the hyperfine field (B_{hf}) for YFe_6Ge_6. Inset shows the Mössbauer spectra at various temperatures.

Since the Mössbauer absorption changes rapidly at zero velocity near the ordering temperature, zero-velocity thermal scans were also used. Finally the heat capacity signature at T_N was observed by DSC and calibrated against a Nickel standard. The results of these measurements are shown in Fig. 5, along with the earlier work of Venturini *et al.* [1]. As with the hyperfine field, there is only a weak dependence on the rare-earth present, and essentially no change in T_N on annealing, whether or not there is a change in crystal structure.

As all of the RFe_6Ge_6 structures are related to the hexagonal (B35) FeGe structure, it is instructive to compare the Mössbauer parameters for these materials. In an annealed FeGe sample at room temperature, we found B_{hf} = 12.1 T with an apparent quadrupole splitting of Δ = 0.34 mm/s in agreement with the measurements of Häggström *et al.* [8]. Point charge model (PCM) calculations (with equal charges on Fe and Ge) show that the principal axis of the electric field gradient (*efg*) lies in the hexagonal ab-plane, while neutron diffraction measurements indicate that the magnetic moments are oriented parallel to the c-axis[7], results that are consistent with the temperature dependence of the Mössbauer parameters [8]. Above T_N we measured Δ = .27(1) mm/s in the RFe_6Ge_6 series, about half that in FeGe (0.60 mm/s [8]), while below T_N Δ is 0.038(6) mm/s, this indicates that the *efg* is substantially reduced in the RFe_6Ge_6 alloys. Furthermore, since PCM calculations (with a charge of +3 on the rare earth atom) indicate that the principal axis of the *efg* remains in the ab-plane, the magnetic easy axis must have changed.

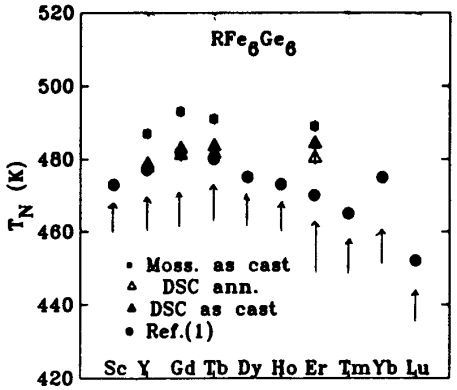

Fig. 5. Néel temperatures (T_N) for as-cast and annealed RFe_6Ge_6 alloys determined by both Mössbauer spectroscopy and DSC. Results from [1] are also shown for comparison.

Acknowledgment

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References

[1] G. Venturini, R. Welter and B. Malaman, *J. Alloys and Compounds* , vol. 185, p. 99, 1992.

[2] B. Chafik El Idrissi, G. Venturini and B. Malaman, *Mat. Res. Bull.* , vol. 26, p. 431, 1991.

[3] B. Chafik El Idrissi, G. Venturini and B. Malaman, *Mat. Res. Bull.* , vol. 26, p. 1331, 1991.

[4] P. Villars, and L.D. Calvert, *Pearson's Handbook of Crystallographic data for Intermetallic Phases*. Materials Park, OH.: American Society of Metals, 1991 2nd edition.

[5] N.M. Belyavina and Y.Ya. Markiv, *Dopov. Akad Nauk. Ukr., RSR Ser.* , vol. B12, p. 30, 1982.

[6] K. Yvon, W. Jeitschko and E. Pathe, *J. Appl. Cryst.* , vol. 10, p. 73, 1977.

[7] J. Bernhard, B. Lebech and O. Beckman, *J. Phys. F* , vol. 14, p. 2379, 1984.

[8] L. Häggström, T. Ericsson, R. Wäppling and E. Karlson, *Phys. Scr.* , vol. 11, p. 55, 1975.