Observation of independent iron and rare-earth ordering in RFe_6Ge_6 (R= *Y*, Gd–Lu) compounds

D. H. Ryan[a] and J. M. Cadogan
School of Physics, The University of New South Wales, Sydney NSW 2052, Australia

Mössbauer and magnetization measurements have been used to study magnetic ordering in RFe_6Ge_6 alloys. The iron sublattice orders antiferromagnetically and T_N remains essentially constant across the series at ~480 K with no evidence of a net magnetization in any of the alloys. For R=Gd−Er, the rare-earth sublattice orders ferromagnetically with T_c's that descend from 30 K at Gd to 3 K at Er. This order is established without affecting the order on the iron sublattice. The large difference in ordering temperatures and the unrelated magnetic structures adopted by the two sublattices indicate that the iron and rare-earth moments are effectively isolated from each other and that they order independently. © *1996 American Institute of Physics.* [S0021-8979(96)13008-3]

INTRODUCTION

Earlier work on RFe_6Ge_6 alloys has shown that they order antiferromagnetically below about 480 K, and that T_N (Ref. 1) is insensitive to the rare-earth element present in the alloy. Furthermore, the hyperfine field at the iron sites, B_{hf}, does not change when Gd or Tb is substituted for *Y*, nor is any net magnetization observed following these substitutions.[2] These results suggest that either the rare-earth sublattice also orders antiferromagnetically, or that it does not order at all.

In order to investigate this alloy series in more detail, we have extended our previous study[2] to include all of the heavy rare earths. We have used Mössbauer spectroscopy to probe, the effects of the rare-earth substitutions on a microscopic scale, and low-temperature susceptibility and magnetization measurements, to look for evidence of magnetic order at the rare-earth sites.

EXPERIMENTAL METHODS

The alloys were prepared by arc-melting stoichiometric ratios of the pure elements (Fe: 99.95%, Ge: 99.999%, and rare-earths: 99.9% pure) under Ti-gettered argon to yield ~2 g ingots. To allow for the inevitable loss of Tm and Yb by evaporation during arc melting, excess Tm (10%) and Yb (25%) was added to the starting mixture. Room temperature Mössbauer spectroscopy showed both the magnetic pattern of the 1–6–6 phase with typically a 10%–20% contamination from the nonmagnetic, tetragonal 1–2–2 phase.[3] Annealing at 900 °C for two weeks sealed under vacuum in quartz tubes yielded single-phase 1–6–6 alloys.

Powder x-ray diffraction patterns were obtained using Cu–K_α radiation on an automated Nicolet–Stoe diffractometer. The structures of the annealed alloys were found to be in agreement with those reported by Venturini *et al.*,[1] with the exception of the Gd alloy where we found no evidence for the superlattice structure and Pnma space group they reported. Our $GdFe_6Ge_6$ alloy showed the much simpler hexagonal P6/mmm structure found also in the Yb and Lu alloys.

Mössbauer spectra were obtained at room temperature in transmission geometry on a conventional constant-acceleration drive using a 1 GBq ^{57}CoRh source. The instrument was calibrated with a natural iron foil and all isomer shifts are given relative to that standard. 60–80 mg samples were hand ground and dispersed in graphite. Resonant absorptions of 7%–10% were obtained.

Thermogravimetric analysis was carried out on a Perkin–Elmer TGA-7 in a small field gradient to look for evidence of ferromagnetic or ferrimagnetic ordering. The Néel temperatures of the alloys were measured on a Perkin–Elmer DSC-7, using the heat capacity peak at T_N as the signature of ordering. Both systems were calibrated using standard alumel and nickel samples. A LakeShore susceptibility system with a closed-cycle refrigerator was used to record χ_{ac} vs T down to 12 K. Magnetization measurements were carried out on a Quantum Design SQUID down to 2 K in fields of up to 5 T.

RESULTS AND DISCUSSION

The room temperature Mössbauer spectra of the annealed samples (Fig. 1) show a magnetically ordered, six-line pattern with a splitting of ~15 T, half that found in α-Fe, suggesting an iron moment of about 1 μ_B. There is no evidence of either magnetic or nonmagnetic contaminants. Thermogravimetric analysis (TGA) measurements showed no sign of either ferromagnetic or ferrimagnetic order between 300 and 600 K. Given the obvious magnetic order on the iron sites observed by Mössbauer spectroscopy, we conclude, as before,[1,2] that the ordering in all of these alloys is antiferromagnetic. The Mössbauer parameters for the alloys studied here are summarized in Fig. 2. The three crystal structures adopted by the alloys in this series are closely related and is it clear from the absence of any jumps in the hyperfine parameters that the local environment of the iron remains essentially unchanged as the structure passes from Cmcm (Y–Ho) through Immm (Er,Tm) to P6/mmm (Yb,Lu). Furthermore, the easy axis of magnetization must remain in the basal plane at room temperature in all of the alloys since the quadrupole splitting is essentially constant across the series.

[a]On leave from Centre for the Physics of Materials and Department of Physics, McGill University, 3600 University St., Montreal, Quebec, Canada.

 0021-8979/96/79(8)/6004/3/$10.00

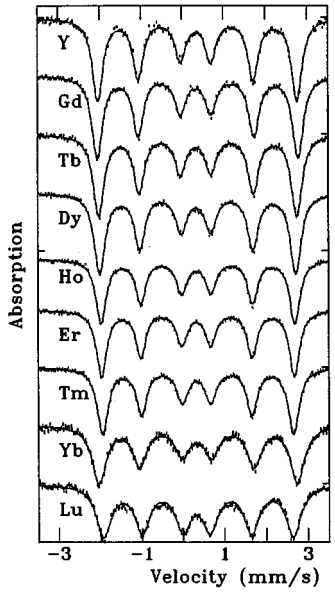

FIG. 1. Room temperature Mössbauer spectra of the annealed RFe_6Ge_6 alloys. Solid lines are fits assuming a single, magnetically ordered iron site.

The most surprising feature of this system is the fact that both the hyperfine field at the iron nucleus ($B_{\rm hf}$, Fig. 2) and T_N (Fig. 3) are essentially independent of the rare-earth present. Apart from a gradual decline in $B_{\rm hf}$ (5%) and T_N (2%) there appears to be no significant change in the magnetic properties on going from Gd to Lu. These results suggest that the rare-earth sublattice does not order with the iron at 480 K, furthermore, an earlier study[1] found no evidence of

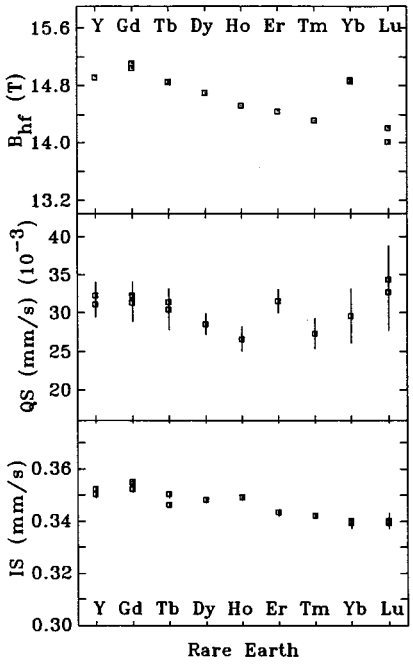

FIG. 2. Summary of fitted hyperfine parameters at room temperature for all of the RFe_6Ge_6 alloys studied here. Error bars are derived from statistical uncertainties. Values obtained from samples before and after annealing are shown in several cases, and agree within error. Data on two Gd alloys are included as a consistency check.

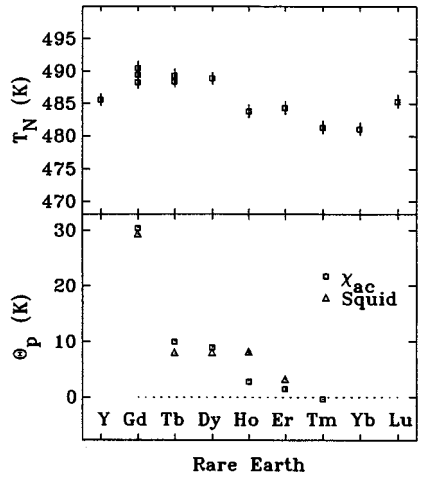

FIG. 3. Top: Néel temperature of the Fe sublattice, derived from DSC measurements. Bottom: Curie–Weiss temperatures for the rare-earth sublattice obtained from fits to $\chi_{\rm ac}$ vs T above 12 K, or SQUID data down to 2 K.

rare-earth ordering down to 90 K. One possible explanation for this behavior could lie in the magnetic structure of the iron sublattice. The ordered state of the binary FeGe compound, from which the 1–6–6 alloys studied here are derived, consists of ferromagnetic Fe planes coupled antiferromagnetically to each other.[4] The 1–6–6 structures are formed by placing rare-earth atoms between the iron planes, and if the magnetic structure of the parent FeGe compound is retained, there could be a net cancellation of the Fe–R exchange at the rare-earth sites, effectively isolating them from the ordering of the iron moments. Since the rare-earth moments do order in RFe_2Ge_2 where the iron atoms carry no moment,[5] it seems reasonable to expect order to develop on the rare-earth sublattice at low enough temperatures. Figure 3 shows paramagnetic ordering temperatures (θ_p) derived from Curie–Weiss fits to $\chi_{\rm ac}$ data measured down to 12 K. Except for the case of $GdFe_6Ge_6$, all of the extrapolated ordering temperatures lie below the limit of the closed-cycle refrigerator, while the value for the Tm alloy is in fact slightly negative. θ_p scales approximately with the deGennes factor for the rare-earths, except for the case of the Tb alloy, where θ_p is too low.

Our data for $GdFe_6Ge_6$ suggest that it orders ferromagnetically at 30.5 ± 0.2 K, giving a large susceptibility that saturates below T_c. This may not be the first observation of ordering in $GdFe_6Ge_6$, as an earlier study of $GdFe_2Ge_2$ showed a susceptibility feature close to this temperature in an off-stoichiometry sample which may have contained some 1–6–6 as an impurity, although no details about phase purity were given.[6] In order to confirm our view of the magnetic structure of the Gd compound, and to determine ordering temperatures for some of the other alloys, we also carried out measurements on a SQUID magnetometer that could be operated down to 2 K. Ordering temperatures, taken from the kink in a plot of $1/\chi$ vs T, are also shown on Fig. 3. These are in agreement with the values extrapolated from 12 K except in the case of the Ho alloy whose ordering temperature is somewhat higher than expected. The magnetization at 2 K, converted to μ_B per formula unit, is shown in Fig. 4

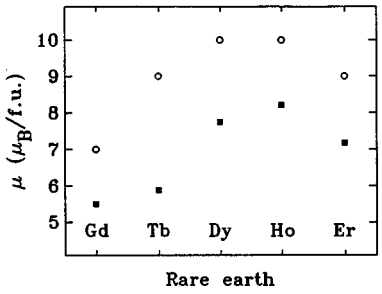

FIG. 4. Ordered moment per formula unit at 2 K (solid symbols) compared with gJ for the corresponding free ion (open symbols) for the RFe_6Ge_6 alloys that ordered above 2 K.

along with values of gJ for each of the rare-earths. A difference of about $2\mu_B$ is apparent in each case. Some of this is clearly due to the measurements being carried out rather closer to T_c than ideal, and a further contribution can be attributed to a failure to saturate the magnetization in 5 T for all of the samples other than $GdFe_6Ge_6$. The origin of the discrepancy remains a problem for the Gd alloy, which was measured at 0.15 T_c and had saturated. Two simple explanations would be either a noncollinear ordering of the Gd sublattice, or an Fe–Gd interaction that modifies the antiferromagnetic order on the Fe sublattice so as to yield a net magnetization directed against that of the Gd sublattice. The high capture cross-section of Gd makes neutron diffraction essentially impossible and so direct structural measurements are not available. Preliminary ^{155}Gd and ^{57}Fe Mössbauer measurements at low temperatures have confirmed that the Gd moments do order at 30 K and that the iron sublattice does not appear to be affected in any way by this ordering.[7]

CONCLUSIONS

Mössbauer and magnetization measurements on RFe_6Ge_6 alloys with $R=Y$, Gd–Lu, indicate that the antiferromagnetic ordering of the iron sublattice at T_N~480 K, is unaffected by changes to the rare-earth element present. Furthermore, the rare-earth sublattice orders ferromagnetically at much lower temperatures, ranging from 30 K for the Gd alloy, to 3 K in the case of Er, without affecting the order on the iron sublattice. The difference in ordering temperature between the iron and rare-earth sublattices, which is never less than a factor of 10, coupled with the unrelated magnetic structures adopted, indicates that the two magnetic species order independently, and that the Fe–R exchange is essentially zero.

ACKNOWLEDGMENTS

We are grateful to S. J. Collocott and C. Andrikidis at CSIRO, Division of Applied Physics, Lindfield NSW, Australia, who made the SQUID measurements. D.H.R. would like to acknowledge the hospitality of the School of Physics at the University of New South Wales, Sydney, Australia where much of this work was carried out. This work was also supported by grants from the Australian Research Council, the Natural Sciences and Engineering Research Council of Canada and Fonds pour la Formation de Chercheurs et l'Aide à la Recherche, Québec.

[1] G. Venturini, R. Welter, and B. Malaman, J. Alloys Comp. **185**, 99 (1992).
[2] Y. B. Wang, D. Wiarda, J. M. Cadogan, and D. H. Ryan, IEEE Trans. Magn. **30**, 4951 (1994).
[3] J. J. Bara, H. U. Hrynkiewicz, A. Milos, and A. Szytula J. Less-Common Met. **161**, 185 (1990).
[4] O. Beckmann, K. Carrender, L. Lundgren, and M. Richardson, Physica Scripta **6**, 151 (1972).
[5] A. Szytula and J. Leciejewicz, in *Handbook on the Physics and Chemistry of the Rare Earths*, edited by K. A. Gschneider, Jr. and L. Eyring (North Holland, Amsterdam, 1989), Vol. 12, p. 133.
[6] F. M. Mulder, R. C. Thiel, and K. H. J. Buschow, J. Alloys Comp. **202**, 29 (1993).
[7] D. H. Ryan, J. M. Cadogan, and J. D. Cashion (unpublished).