JOURNAL OF APPLIED PHYSICS VOLUME 93, NUMBER 10 15 MAY 2003

Noncollinearity of the magnetic structure of $TbFe_{10}V_2$

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

D. H. Ryan
Department of Physics and Centre for the Physics of Materials, McGill University, Montreal, Canada H3A 2T8

O. Moze
Istituto Nazionale per la Fisica della Materia, Dipartimento di Fisica, Università di Modena e Reggio Emilia, Via G. Campi 213/a, I-41100, Modena, Italy

I. P. Swainson
Neutron Programme for Materials Research, Steacie Institute for Molecular Sciences, National Research Council, Chalk River Laboratories, Ontario, Canada K0J 1J0

K. Suzuki
School of Physics and Materials Engineering, Monash University, Clayton, Victoria, Australia

(Presented on 12 November 2002)

We have studied the $ThMn_{12}$-type compound $TbFe_{10}V_2$ by magnetometry and high-resolution neutron powder diffraction. Previous workers claimed that $TbFe_{10}V_2$ undergoes a spin reorientation away from the tetragonal *c* axis at around 200 K, with the collinear magnetization eventually reaching an angle of 50° at 4 K. We have reinvestigated $TbFe_{10}V_2$ due to the unusual temperature dependence of its magnetization. We show that this behavior cannot be explained by a compensation effect and we suggest that a canted, noncollinear magnetic structure develops below the spin-reorientation temperature. [DOI: 10.1063/1.1556162]

I. INTRODUCTION

The tetragonal $ThMn_{12}$ structure is the basis for numerous rare-earth (R)—transition-metal intermetallic compounds, some of which show potential for permanent-magnet application after interstitial modification with nitrogen or carbon. The space group is $I4/mmm$ (No. 139) and there are two formula units (f.u.) per unit cell. The site occupancies are $2a$ for Th (and R) and $8f$, $8i$, and $8j$ for Mn (and Fe). Binary RFe_{12} compounds do not form and a third element is required to stabilize this structure. To date, $RFe_{12-x}M_x$ compounds have been formed with M=Ti, V, Cr, Mn, Nb, Mo, W, Re, Al, and Si. From a fundamental viewpoint, the $R(Fe,M)_{12}$ compounds provide much useful information on the crystal-field interactions at the R^{3+} ion, the R–Fe and Fe–Fe exchange interactions, and the complex interplay between the crystal field and the exchange, manifesting as spin reorientations which occur in many $R(Fe,M)_{12}$ compounds at low temperatures. Such changes in the magnetic structure are generally due to either (i) competition between the R and Fe anisotropies and/or (ii) competition between the second, fourth, and sixth order terms in the R^{3+} crystal field, with the higher-order terms playing a more significant role as $T \rightarrow 0$. In this article we present a study of the magnetic structure of $TbFe_{10}V_2$ using magnetometry and high-resolution neutron powder diffraction. $TbFe_{10}V_2$ is magnetically ordered along [001] below 570 K and undergoes a gradual spin reorientation away from [001] below 170 K.[1,2] We have confirmed these critical temperatures. However, unlike in previous reports[3,4] where the magnetic structure remains collinear in the canted regime, we suggest that the magnetic structure at low temperatures is in fact noncollinear.

II. EXPERIMENTAL METHODS

The $TbFe_{10}V_2$ sample was prepared by arc-melting stoichiometric amounts of the pure elements under Ti-gettered argon, allowing a 2 wt% excess of Tb to compensate for the inevitable boiloff during melting. The arc-melted ingot was annealed at 900 °C for two weeks, sealed under vacuum in a quartz tube. Powder x-ray diffraction was carried out using Cu K_α radiation on an automated Nicolet–Stoe diffractometer. Magnetometry measurements were made on a Quantum Design PPMS.

Neutron powder diffraction experiments were carried out on the DUALSPEC C2 high-resolution diffractometer at the NRU reactor, Chalk River Laboratories, operated by Atomic Energy Canada Ltd. The neutron wavelength was 2.3685 (1) Å. A review of the neutron scattering facilities at Chalk River, including a description of C2, can be found in Ref. 5. Fifteen diffraction patterns were obtained over the temperature range 8–200 K and all patterns were analyzed using the Rietveld method and the FULLPROF program.[6]

III. RESULTS AND DISCUSSION

The annealed sample of $TbFe_{10}V_2$ was virtually single-phase $ThMn_{12}$ type with ~5 wt% of α-Fe(V) present, as

---

[a)] Author to whom correspondence should be addressed; electronic mail: j.cadogan@unsw.edu.au

0021-8979/2003/93(10)/6972/3/$20.00

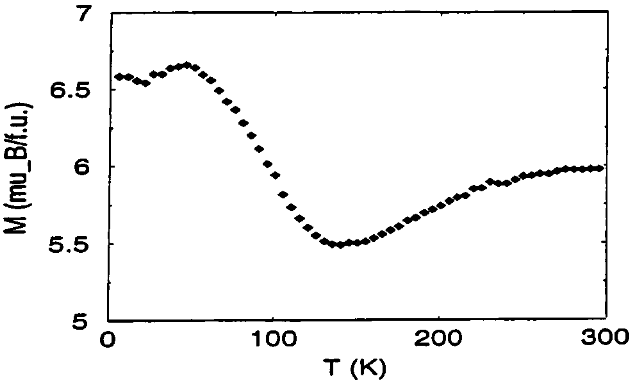

FIG. 1. Temperature dependence of the magnetization of a $\mathrm{TbFe}_{10}\mathrm{V}_2$ ingot in 1.25 T.

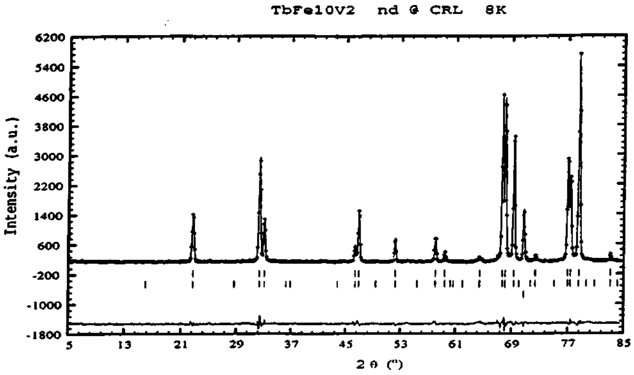

FIG. 2. Neutron powder diffraction pattern of $\mathrm{TbFe}_{10}\mathrm{V}_2$ obtained at 8 K. The Bragg position markers are for $\mathrm{TbFe}_{10}\mathrm{V}_2$ [nuclear (top), magnetic (middle)] and the α-Fe(V) impurity (bottom).

determined from the fits to the neutron diffraction patterns. In Fig. 1 we show the temperature dependence of the magnetization of $\mathrm{TbFe}_{10}\mathrm{V}_2$, measured on an ingot in a magnetic field of 1.25 T. The low-temperature magnetization of this polycrystalline ingot is $\sim 6.6\,\mu_B$/f.u. which yields an intrinsic formula unit magnetization of $\sim 13.2\,\mu_B$/f.u., assuming the simple standard averaging factor of 1/2. In agreement with de Boer *et al.*[7] the magnetization of $\mathrm{TbFe}_{10}\mathrm{V}_2$ first decreases upon heating from $T \sim 0$ K, passing through a minimum around 150 K. Such behavior is reminiscent of the compensation effect commonly observed in R–Fe ferrimagnets. However, in the case of $\mathrm{TbFe}_{10}\mathrm{V}_2$, compensation cannot occur since the Fe sublattice magnetization is more than double that of the Tb sublattice (see Table I). The Tb^{3+} "free-ion" moment is 9 μ_B and Tb^{3+} has a "spin" of $J=6$ so the temperature dependence of its magnetic moment is much more rapid than that of the Fe (see Fig. 3). We suggest, therefore, that the magnetic structure of $\mathrm{TbFe}_{10}\mathrm{V}_2$ below 170 K cannot be collinear.

In Fig. 2 we show the neutron diffraction pattern of $\mathrm{TbFe}_{10}\mathrm{V}_2$ obtained at 8 K, i.e., in the canted regime. It is well established from neutron diffraction and Mössbauer work that most of the 1:12-stabilizing elements show a strong preferential occupation of the $8i$ site and our neutron work confirms that the V exclusively occupies the $8i$ site.

TABLE I. Lattice parameters, atomic positions, and magnetic moments (in μ_B), magnetization, and canting angles of $\mathrm{TbFe}_{10}\mathrm{V}_2$ deduced from the fit to the 8 K neutron diffraction pattern.

a(Å)	c (Å)	$x(8j)$	$x(8i)$
8.5026(5)	4.7848(3)	0.276(1)	0.359(1)
	Noncollinear model		
μ(Tb)	μ(Fe$-8f$)	μ(Fe$-8j$)	μ(Fe$-8i$)
−8.96(17)	1.88(10)	2.05(12)	2.38(15)
M(μ_B/f.u.)	θ'(Tb)	θ(Fe)	
12.8(7)	37.8(70)	13.8(50)	
	Collinear model		
μ(Tb)	μ(Fe$-8f$)	μ(Fe$-8j$)	μ(Fe$-8i$)
−8.87(17)	1.64(8)	1.98(9)	2.16(13)
M(μ_B/f.u.)	θ(Tb)	θ(Fe)	
9.9(11)	31.4(60)	31.4(60)	

The refined atomic and magnetic parameters are given in Table I. The refinement "R factors (%)" for all 15 patterns obtained during this study lie within the ranges: R(Bragg) =2.3–4.5, R(F structure)=1.9–3.0, R(wp)=9.4–12.1, R(exp)=4.4–4.7 and R(mag)=3.3–6.1. In agreement with previous Mössbauer and neutron work, we find that the largest Fe magnetic moment is associated with the $8i$ site.

The fit to the 8 K neutron pattern also suggests that the Tb and Fe magnetic moments may be slightly larger in the noncollinear structure than the collinear structure, although the differences are quite small and within experimental error. Nevertheless, the noncollinear model allows the Tb and Fe sublattices to approach their individual easy magnetization directions (EMD) more closely and orbital effects would therefore be expected to augment the overall moment of each atom. The magnetocrystalline anisotropy of the Fe sublattice in the $\mathrm{R(Fe,M)}_{12}$ compounds is $K_1^{\mathrm{Fe}}(T=0) \sim +24$ K/f.u., using standard notation, thus favoring the [001] direction. The overall low-temperature anisotropy of the Tb sublattice arising from the second, fourth, and sixth order terms in the Tb^{3+} crystal field favors a non-[001] EMD as illustrated by the observation of a spin reorientation. Unfortunately, we must note that the analysis of the neutron diffraction patterns failed to provide conclusive evidence for a noncollinear magnetic structure as the differences between the noncollinear and collinear fits are small.

Our calculated magnetization value of $12.8\,\mu_B$/f.u. in the noncollinear model compares well with our experimentally determined value of $13.2\,\mu_B$/f.u.

IV. MAGNETOCRYSTALLINE ANISOTROPY

The magnetocrystalline anisotropy of the R^{3+} sublattice in $\mathrm{R(Fe,M)}_{12}$ is determined by the crystal-field Hamiltonian appropriate to the $4/mmm$ point symmetry of the R^{3+} site

$$\mathcal{H}_{\mathrm{cf}} = B_{20}O_{20} + B_{40}O_{40} + B_{44}O_{44} + B_{60}O_{60} + B_{64}O_{64} \qquad (1)$$

using standard notation.

The case of the crystal field acting on the Tb^{3+} ion in $\mathrm{TbFe}_{10}\mathrm{V}_2$ remains an unresolved controversy. Christides *et al.*[1,2] reported a study of the crystal field and spin reorientations in the $\mathrm{RFe}_{10}\mathrm{V}_2$ and $\mathrm{RFe}_{10}\mathrm{Si}_2$ series, for R=Nd, Tb, Dy, Ho, Er, and Tm. They found that the general magnetic

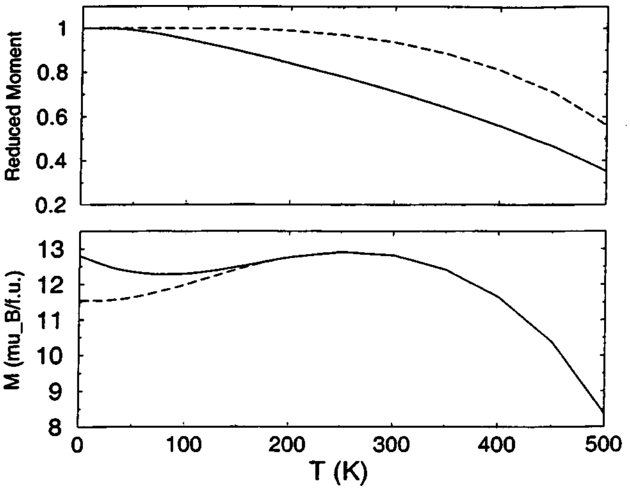

FIG. 3. Upper: reduced magnetization of Tb (full line) and Fe (dashed line) sublattices in $TbFe_{10}V_2$. Lower: simulated magnetization temperature dependence of $TbFe_{10}V_2$ for the noncollinear (full line) and collinear (dashed line) models.

behavior of each series could be reproduced with a single set of crystal-field coefficients, appropriate to that series, with the glaring exception of $TbFe_{10}V_2$. Such a discrepancy was also observed in the $RFe_{11}Ti$ series by Hu *et al.*[8] and both groups suggested that the failure of the crystal-field approach in the case of R=Tb may be due to an admixture of the Tb^{4+} state with the Tb^{3+} state. Curiously, though, Christides *et al.*[1,2] were able to explain the behavior of $TbFe_{10}Si_2$ with the same crystal-field coefficients as the rest of the $RFe_{10}Si_2$ series. The crystal-field parameters deduced for the $TbFe_{10}Si_2$ are inapplicable to $TbFe_{10}V_2$ since Si, unlike either V or Ti, shows preferential occupation of the $8f$ and $8j$ sites, rather than the usual $8i$ site preference, with a concomitant effect on the Tb^{3+} crystal field.

Abadia *et al.*[9] determined crystal-field parameters for $TbFe_{11}Ti$ from single-crystal measurements but these are inapplicable to $TbFe_{10}V_2$ since the EMD of $TbFe_{11}Ti$ is along [100] over the entire temperature range 4–300 K, whereas $TbFe_{10}V_2$ has easy [001] in the range $T > 170$ K and only cants towards the (001) plane as $T \rightarrow 0$ K.

We suggest that the failure of the general crystal-field coefficients within a series to explain the magnetic behavior of both $TbFe_{10}V_2$ and $TbFe_{10}Si_2$ may be related to the preferential site occupancy of the stabilizing element in $Tb(Fe,M)_{12}$ whereby Tb–M hybridization could lead to valence instability and the admixture of the half filled $Tb^{4+}(4f^7)$ S state.

In Fig. 3 we show the reduced magnetizations of the Tb and Fe sublattices, calculated using a simple molecular field approach, as outlined in Ref. 10. Using ordering temperatures of 570 and 532 K for $TbFe_{10}V_2$ and $YFe_{10}V_2$, respectively, we calculate molecular fields (at $T=0$) of 655, 143, and 80 T, characterizing the Fe→Fe, Fe→Tb, and Tb→Fe interactions, respectively. In Fig. 3 we also show the simulated magnetization temperature dependence of $TbFe_{10}V_2$ for the noncollinear and collinear models, using the data given in Table I. The collinear, canted model exhibits typical Néel ferrimagnetic behavior whereas the noncollinear model shows the noncompensation minimum observed experimentally. However, the case of $TbFe_{10}V_2$ remains problematic. For example, the maximum noncollinearity of 24° is difficult to reconcile with the fact that the R–Fe exchange energy clearly dominates the magnetocrystalline anisotropy in $R(Fe,M)_{12}$ compounds.

ACKNOWLEDGMENTS

This work was supported by the Australian Academy of Sciences, the Australian Nuclear Science and Technology Organization, the Natural Sciences and Engineering Research Council of Canada, Fonds pour la formation de chercheurs et l'aide à la recherche, Québec, and Istituto Nazionale per la Fisica della Materia, Italy.

[1] C. Christides, D. Niarchos, H. S. Li, A. Kostikas, B. P. Hu, and J. M. D. Coey, Solid State Commun. **72**, 839 (1989).
[2] C. Christides, M. Anagnostou, H. S. Li, A. Kostikas, and D. Niarchos, Phys. Rev. B **44**, 2182 (1991).
[3] R. B. Helmholdt, J. J. M. Vleggaar, and K. H. J. Buschow, J. Less-Common Met. **144**, 209 (1988).
[4] W. G. Haije, J. Spijkerman, F. R. de Boer, K. Bakker, and K. H. J. Buschow, J. Less-Common Met. **162**, 285 (1990).
[5] B. M. Powell, Neutron News **1**, 16 (1990).
[6] J. Rodríguez-Carvajal, Physica B **192**, 55 (1995).
[7] F. R. de Boer, Y. K. Huang, D. B. de Mooij, and K. H. J. Buschow, J. Less-Common Met. **135**, 199 (1987).
[8] B. P. Hu, H. S. Li, J. M. D. Coey, and J. P. Gavigan, Phys. Rev. B **41**, 2221 (1990).
[9] C. Abadía, P. A. Algarabel, B. Garcia-Landa, M. R. Ibarra, A. del Moral, N. V. Kudrevatykh, and P. E. Markin, J. Phys.: Condens. Matter **10**, 349 (1998).
[10] J. M. Cadogan, J. P. Gavigan, D. Givord, and H. S. Li, J. Phys. F: Met. Phys. **18**, 779 (1988).