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TbFe₂, a rhombohedral Laves phase.* By A.E.DWIGHT and C.W.KIMBALL, *Department of Physics, Northern Illinois University, DeKalb, Illinois 60115, U.S.A.*

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Rhombohedral, $R\bar{3}m$, $a_R = 5.207$ (2) Å, $\alpha = 59.62$ (2)°, $a_H = 5.189$ (2), $c_H = 12.821$ (4) Å, $Z = 2$. Tb in 2(c) ($x = \frac{1}{8}$), Fe in 1(b) and 3(e) sites. The normal MgCu₂-type structure is distorted by an elongation along the [111] direction. Dependence of distortion on composition was studied in Tb(Fe_{1-x}Al_x)₂, Tb(Fe_{1-x}Co_x)₂ and (Y_{1-x}Tb_x)Fe₂ ternary compounds.

Introduction

Clark & Belson (1972) and Koon, Schindler & Carter (1971) describe giant room-temperature magnetostrictive effects in TbFe₂, but do not report the distorted crystal structure. Buschow & van Stapele (1970) report a MgCu₂-type structure, $a = 7.351$ Å.

Experimental

Arc-melted alloys were homogenized at 800°C. Debye-Scherrer patterns with filtered Co, Fe and Cr radiation showed line-splitting in high-angle reflections. By graphical methods hexagonal indices were obtained, for a cell with three times the volume of the primitive rhombohedral cell. Computer programs were used to calculate intensities (Yvon, Jeitschko & Parthé, 1969) and to refine cell constants (Muel-ler, Heaton & Miller, 1960).

To confirm the structure, step-scan data were obtained with a General Electric Company diffractometer using filtered Co radiation for the cubic 731 and 642 reflections. A least-squares routine was used to fit a calculated profile of the multi-indexed peak.

* Based on work performed under the auspices of the National Science Foundation.

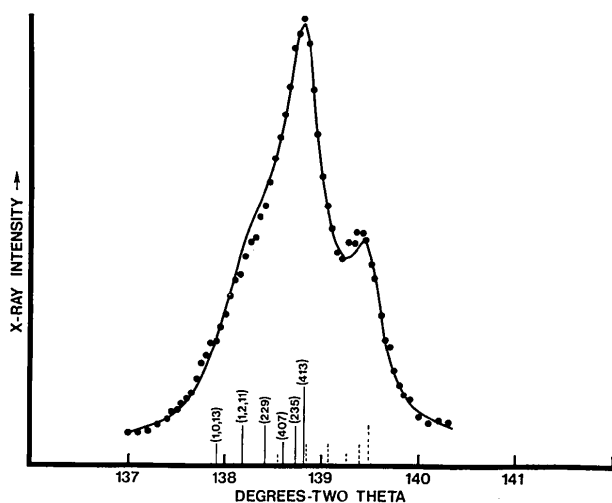


Fig. 1. Data points obtained by step scanning, and the calculated profile of the 'cubic' 731 reflection (actually six closely spaced hexagonal reflections).

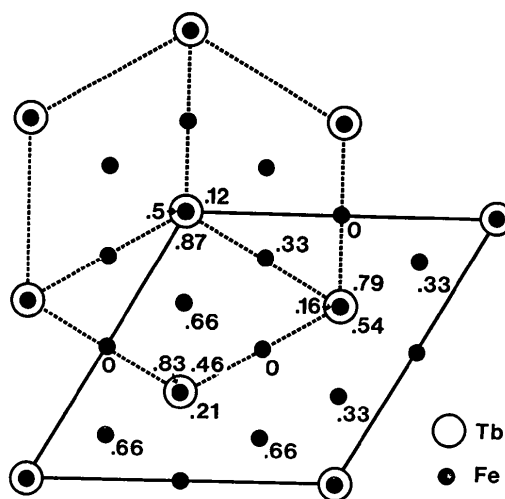


Fig. 2. Relation between the primitive rhombohedral and tripled hexagonal unit cells of TbFe₂.

Results

Fig. 1 shows the data points obtained by step scanning and the calculated profile of the 731 reflection. Indices, d

Table 1. Observed and calculated d spacings and intensities for hexagonal (rhombohedral) TbFe₂, Debye-Scherrer film, Co K α radiation

The abbreviation n.o. = not observed

Cubic	Hexagonal	Rhomb.	d_o	d_c	I_o	I_c
hkl	HKL	hkl				
111	{ 003 101	111 010	4.21	4.2738 4.2413	m	125 367
200	{ 012 101	012 101	n.o.	3.680	n.o.	0
220	{ 104 110 015	211 10 $\bar{1}$ 221	2.59	2.6096 2.5948 2.2272	S	1000 984 725
331	{ 113 021	201 11 $\bar{1}$	2.205	2.2180 2.2134	VS	1431 711
222	{ 006 202	222 200	2.11	2.1369 2.1206	w	98 287
400	{ 024 107	022 322	n.o.	1.840 1.6962	n.o.	28 33
331	{ 205 211	311 01 $\bar{2}$	1.68	1.690 1.684	vw	33 65

Table 1 (cont.)

420	116	132		1.6495		0
	122	12 $\bar{1}$	n.o.	1.642	n.o.	0
422	018	332	1.502	1.5096	w	185
	214	301		1.5009		363
	300	11 $\bar{2}$	1.50	1.4981	S	181
551	009	333		1.4246		58
	027	133		1.4197		171
333	125	320	1.416	1.4161	S	340
	303	22 $\bar{1}$		1.4138		340
440	208	242	1.301	1.3048	S	352
	220	20 $\bar{2}$	1.298	1.2974	S	347
531	119	432		1.2488		30
	217	241		1.2455		30
	223	31 $\bar{1}$	1.241	1.2415	vw	30
442	131	21 $\bar{2}$		1.2407		30
	1,0,10	433		1.2329		0
600	306	114	n.o.	1.2267	n.o.	0
	312	301		1.2236		0
620	128	431	1.163	1.1657	m	206
	134	32 $\bar{1}$	1.161	1.1617	S	206
533	0,1,11	344	1.122	1.1282	w	111
	315	401		1.1211		222
	401	11 $\bar{3}$	1.119	1.1193	S	111
622	0,2,10	442		1.1136		46
	226	042	1.107	1.1090	m	93
	042	22 $\bar{2}$		1.1067		46
444	0,0,12	444	n.o.	1.0684	n.o.	4
	404	400	n.o.	1.0603	n.o.	11
	2,0,11	533	n.o.	1.0347	n.o.	15
551	309	522		1.0327		30
	137	403		1.0305		30
711	045	33 $\bar{1}$	1.028	1.0291	w	15
	321	03 $\bar{2}$		1.0278		30
640	2,1,10	532	n.o.	1.0234	n.o.	0
	232	13 $\bar{2}$	n.o.	1.0180	n.o.	0
	1,1,12	543		0.9880		258
642	318	512	0.984	0.9839	m	264
	324	41 $\bar{1}$		0.9815		268
	410	12 $\bar{3}$	0.981	0.9807	S	270
553	1,0,13	544		0.9633		163
	1,2,11	542	0.958	0.9611	m	332
	229	531		0.9592		336
731	407	511		0.9577		171
	235	24 $\bar{1}$	0.9555	0.9566	S	172
800	143	23 $\bar{2}$		0.9559		693
	048	440	0.9188	0.920	m	702
	0,2,13	553	n.o.	0.9031	n.o.	76
	327	205		0.8985		220
	051	223		0.8967		148

spacings and intensities are given in Table 1. A projection of the hexagonal and rhombohedral cells is shown in Fig. 2.

Ternary alloys were made in which Y, Co or Al, singly, were substituted into TbFe₂. With increasing Al substitution, the volume per formula weight (*V/M*) increased, but the distortion decreased (Fig. 3) until at Tb(Fe_{0.75}Al_{0.25})₂ the structure became the normal MgCu₂ type.

When Tb is partially replaced with Y (Fig. 4), the *V/M* remains nearly constant, and the distortion decreases, so that the structure becomes cubic at approximately Tb_{0.25}Y_{0.75}Fe₂. In a third series of ternary alloys (Fig. 5) Co replaced part of the Fe. The rhombohedral distortion persists in most of the series, becoming zero at approximately Tb(Fe_{0.1}Co_{0.9})₂. The *V/M* decreases with increasing Co. No increase in cell volume between 5 and 10 at. % Co substitution was observed, as in the case reported by Mansey, Raynor & Harris (1968) for the ErFe₂-ErCo₂ system.

Discussion

The rhombohedral distortion in 'cubic' lanthanide compounds may be peculiar to Tb compounds, as the normal MgCu₂-type structure was found in GdFe₂ and DyFe₂, and other lanthanide-Fe₂ alloys. Busch & Levy (1970) reported rhombohedral distortion in TbP, TbAs and TbSb, but tetragonal distortion in DyP, DyAs and DySb. The rhombohedral distortion exists at less than 17K; at higher temperatures the compounds have the NaCl-type structure.

In an investigation of perovskite structures, Jacobson, Tofield & Fender (1973) reported BaTbO₃ to be rhombohedral with $\alpha = 60^\circ 22'$. They offer the explanation that rare-earth ions are slightly too large to stabilize a perfectly cubic perovskite structure. This explanation cannot be valid for the deformed cubic structure of TbFe₂, because the larger Gd ion forms a normal MgCu₂-type structure. Moreover, we shall report elsewhere (Kimball, Dwight, Preston & Taneja, 1974) on corroborative evidence that the distortion in the TbFe₂-YFe₂ system is related to the magnetic properties.

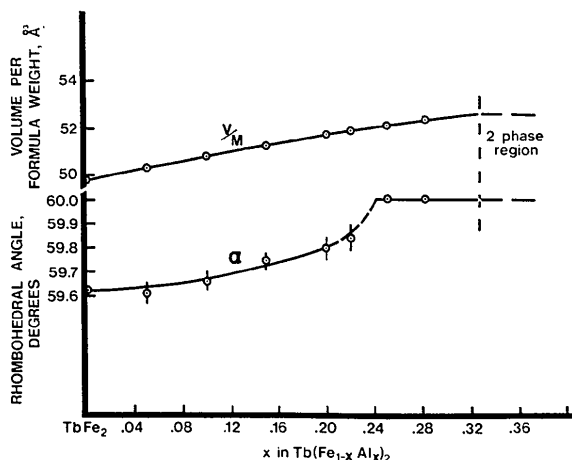


Fig. 3. *V/M* and α in Tb(Fe_{1-x}Al_x)₂ alloys with increasing Al substitution.

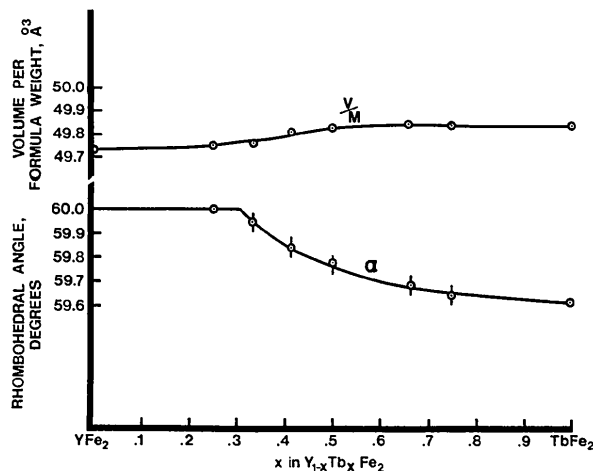


Fig. 4. *V/M* and α in Y_{1-x}Tb_xFe₂ alloys with increasing Tb substitution.

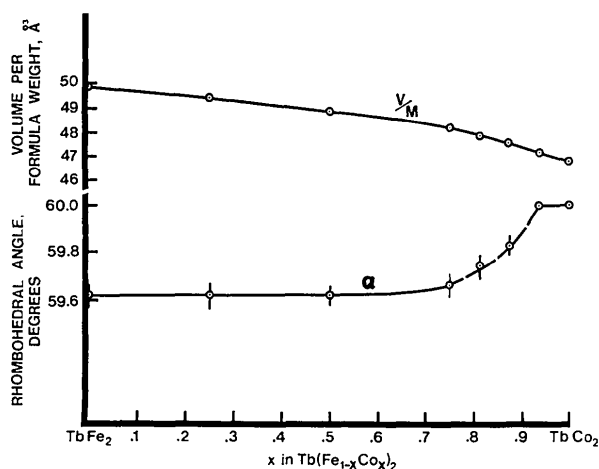


Fig. 5. V/M and α in $Tb(Fe_{1-x}Co_x)_2$ alloys with increasing Co substitution.

A rhombohedral distortion of a cubic structure in $Tb_3Fe_5O_{12}$ at 6.75K has been reported by Tcheou, Bertaut, Delapalme, Sayetat & Fuess (1970). These authors have discussed the magnetic ordering of the Tb and Fe moments and its relationship to the crystal structure.

Although Tb is the only lanthanide with compounds that exhibit rhombohedral distortion, actinide compounds are known that distort rhombohedrally at low temperatures (below their Curie temperature). Examples are US and USE (Marples, 1970) and NpN (Lander & Mueller, 1973).

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