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LETTER TO THE EDITOR

Structural and magnetic characterization of the new ternary phase $Tb_3(Fe_{1-x}Ti_x)_{29}$

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Abstract. We report the existence and characterization of the stable ternary phase $Tb_3(Fe_{1-x}Ti_x)_{29}$. The structural characterization by x-ray powder diffraction is evidence for a monoclinic structure ($P2_1/c$ space group) with refined lattice parameters $a = 10.583(1)$ Å, $b = 8.5116(7)$ Å, $c = 9.6736(9)$ Å and $\beta = 97.018(5)°$. A large magnetovolume effect has been observed in the volume thermal expansion at the order temperature $T_c = 455$ K. The anisotropy has been measured by using the singular point detection technique. Two distinct anisotropy fields of relatively high intensity have been detected. The H_A values measured at 6.4 T and 1.9 T at 293 K and both increase markedly with decreasing temperature. Below 200 K, the approach to saturation corresponding to the highest H_A develops into a first-order magnetization process.

A novel family of ternary intermetallic compounds was recently discovered at the iron-rich edge of the R–Fe (R = rare earth) phase diagram. The addition of Ti is necessary in order to stabilize the phase $R_3(Fe_{1-x}Ti_x)_{29}$ [1–4] with $x \simeq 0.04$–0.06. Careful crystallographic studies using x-ray [5] and neutron diffraction [6] on $Nd_3(Fe_{1-x}Ti_x)_{29}$ have undoubtedly established the 3:29 ratio as an intermediate structure between 2:17 and 1:12, all of them derived from different dumbbell substitutions in the $CaCu_5$ structure. Recent thermal expansion, AC initial magnetic susceptibility and singular point detection (SPD) measurements [7, 8] have characterized the $Nd_3(FeTi)_{29}$ compound thermally and magnetically. A large magnetovolume effect was observed with a large spontaneous volume magnetostriction at low temperature ($\omega_s = 0.74\%$) [8] and a linear dependence of T_c under hydrostatic pressure of $dT_c/dp = -2.9$ K kbar^{-1} [9]. A spin reorientation transition was observed at 233 K, which was identified as easy plane towards easy cone at low temperature [7]. Below 100 K, the approach to saturation along a direction in the basal plane develops in a FOMP (first-order magnetization process) [7, 8]. The close crystallographic relation with the 1:12 structure suggested a careful study in both phases [10]. The new phase 3:29 is formed with the rest of the light rare earth ions. The compound with yttrium does not exist, and in our attempts to prepare it, starting from the same nominal composition and following a similar annealing process we obtained the 2:17 phase. In the case of gadolinium the

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situation is not clear at present. Fuerst *et al* [11] reported the non-existence of $Gd_3(FeTi)_{29}$, however Li *et al* [5] found such a phase. Preliminary attempts in obtaining this phase in our laboratory were unsuccessful. Nevertheless, we succeeded in the preparation of the compound $Tb_3(FeTi)_{29}$, which previously to our knowledge had not been obtained. We report in this paper a structural and magnetic characterization of this novel compound.

The polycrystalline samples were prepared from high-purity Tb (3N) and Fe, Ti (4N) components using an argon-arc furnace. The samples were annealed at 1100 °C under an argon atmosphere for three days and then water quenched. Small amounts of α-Fe and $Tb(FeTi)_{12}$ were detected by thermomagnetic analysis.

Step scanned powder x-ray diffraction was performed at room temperature in a Dmax-B Rigaku system using Cu Kα radiation from a rotating anode. The system was operated at 45 kV and 100 mA covering an angular interval between 18° and 100° in 2θ with an angular step of 0.02° and a counting rate of 6 s/step. The crystallographic structure was refined by the full pattern Rietveld method using the FULLPROF program. An overall temperature factor was used and a pseudo-Voigt function was selected as the peak shape function. The atomic positions for the related phase $Nd_3(FeTi)_{29}$ [6] were used as starting parameters in the refinement process and as a first approximation we have ignored the presence of the Ti atoms.

Thermal expansion experiments were performed using a 'push-rod' method in the temperature range 150–550 K. SPD measurements were carried out using a high pulsed magnetic field up to 35 T in the temperature range 77–300 K. The AC initial magnetic susceptibility was measured again using a mutual inductance Hartshorn bridge with an excitation field of $\simeq$30 mOe of peak value at a frequency of 15 Hz.

Structural characterization. The x-ray pattern of $Tb_3(FeTi)_{29}$, plotted in figure 1, shows an identical shape to the recently reported one for $Nd_3(FeTi)_{29}$, indicating the same crystallographic structure for the two compounds. As a consequence, we have performed the structural study assuming a monoclinic structure with the space group $P2_1/c$ characteristic of this 3:29 phase [4–6]. In figure 1 we have plotted the best fit obtained and in table 1 the structural parameters are summarized including the reliability factors obtained. These results confirm the existence of the 3:29 phase as well as the monoclinic symmetry of the unit cell for the $Tb_3(FeTi)_{29}$ compound. The fractional atomic positions and the unit cell parameters agree reasonably with those reported for $Nd_3(FeTi)_{29}$ [5, 6]. It can be noted that the lattice parameters and cell volume are slightly smaller for Tb than for Nd ions in agreement with the lanthanide contraction. In the first step of the refinement, the isotropic temperature factors for all the atoms were fixed at a value of $B = 0.5$. The final overall temperature factor is 0.1(1) which could arise from the effect of the ignored Ti atoms. Low values of the overall temperature factor have also been reported in the isomorphous $Nd_3(FeTi)_{29}$ [5].

Thermal expansion. The linear thermal expansion (LTE) and the LTE coefficient, α, are displayed in figure 2. A very well defined anomaly is observed at $T_c = 455(5)$ K which is associated with the magnetic ordering temperature. Below this temperature an extra contribution of magnetic origin produces an Invar-like behaviour. In order to evaluate the spontaneous volume magnetostriction, $\omega_s(T)$, we have to obtain the non-magnetic anharmonic phonon contribution, $(\Delta l/l)_{nm}$. We have obtained this contribution (dashed line in figure 2) from the Grüneisen relation $\alpha_{nm}(T) = \kappa\gamma C_v/3$, where κ is the isothermal compressibility constant ($\kappa = 9.5 \times 10^{-4}$ kbar^{-1} [9]), γ is the Grüneisen parameter and C_v the specific heat. We have calculated the thermal dependence of the C_v using a fixed Debye temperature $\theta_D = 450$ K [8]. From these results we have calculated $(\Delta l/l)_{nm}$, fitted in the paramagnetic phase to the experimental results. ω_s was calculated as $\omega_s = 3(\Delta l/l)_s$ with

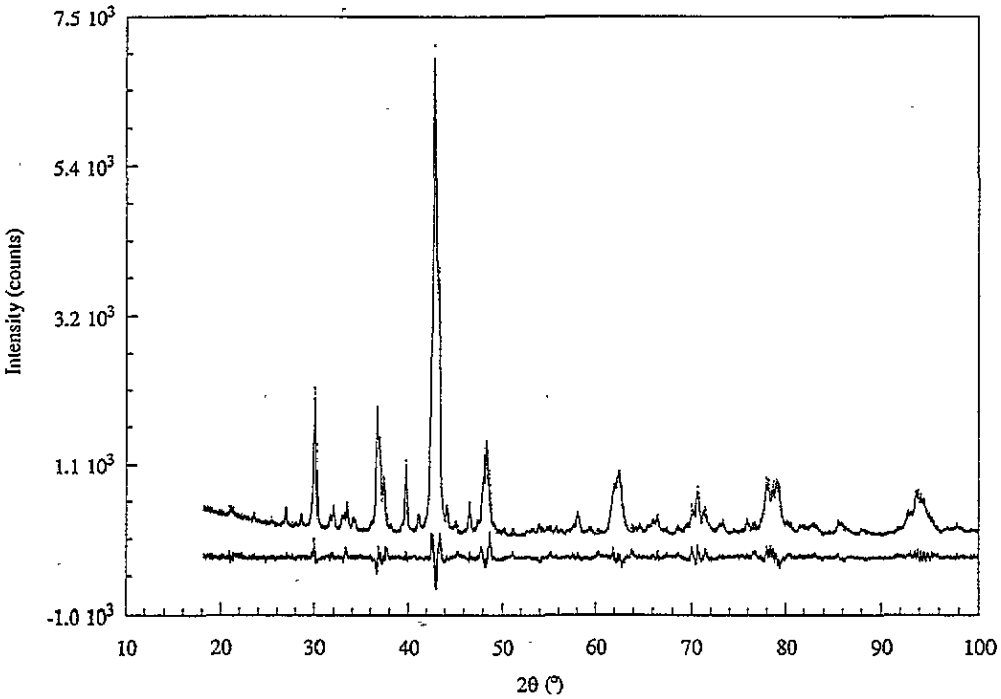

Figure 1. Experimental (dots) and calculated (solid line) x-ray diffraction profiles for $Tb_3(Fe_{0.96}Ti_{0.04})_{29}$. The residual is plotted at the bottom.

Table 1. Refined fractional atomic positions and lattice parameters of $Tb_3(Fe_{0.96}Ti_{0.04})_{29}$ obtained from the powder x-ray diffraction pattern.

Space group: $P2_1/c$		Cell volume = 864.8 Å^3	$Z = 2$	
Atom	Site	x	y	z
Tb	2a	0	0	0
Tb	4e	0.404(1)	−0.011(1)	0.812(1)
Fe	2d	$\frac{1}{2}$	0	$\frac{1}{2}$
Fe	$4e_1$	0.111(1)	0.000(3)	0.730(1)
Fe	$4e_2$	0.297(2)	0.003(3)	0.091(2)
Fe	$4e_3$	0.248(2)	0.017(3)	0.518(1)
Fe	$4e_4$	0.140(2)	−0.002(4)	0.289(2)
Fe	$4e_5$	0.621(3)	0.134(3)	0.683(2)
Fe	$4e_6$	0.804(2)	0.206(3)	0.074(2)
Fe	$4e_7$	0.597(2)	0.249(4)	0.427(2)
Fe	$4e_8$	−0.006(3)	0.248(4)	0.253(3)
Fe	$4e_9$	0.415(2)	0.250(3)	0.052(2)
Fe	$4e_{10}$	0.785(2)	0.254(3)	0.850(2)
Fe	$4e_{11}$	0.194(2)	0.249(4)	0.163(2)
Fe	$4e_{12}$	0.195(2)	0.272(2)	0.401(2)
Fe	$4e_{13}$	0.384(2)	0.344(3)	0.816(2)
Fe	$4e_{14}$	0.001(3)	0.353(2)	0.816(2)
a = 10.583(1) Å	b = 8.5116(7) Å	c = 9.6736(9) Å	β = 97.018(5)°	
R_p = 7.5%	R_{wp} = 9.9%	R_{exp} = 5.1%	R_{Bragg} = 5.6%	

$(\Delta l/l)_s = (\Delta l/l)_{exp} - (\Delta l/l)_{nm}$, where $(\Delta l/l)_{exp}$ is the measured LTE. A considerable value of ω_s is observed even in the paramagnetic phase, which indicates the existence of strong short-range magnetic correlations. A large value of ω_s at low temperatures ($\omega_s(0) \simeq 1.3\%$) has been estimated. This large effect cannot be interpreted as solely originating from the dependence of the exchange integral on distance as we initially proposed in the case of the $Nd_3(FeTi)_{29}$ compound, but also the effect of volume on the 3d sublattice magnetic moment should be considered in these compounds. We have recently reported a detailed description of the Invar effect in these and related compounds [8].

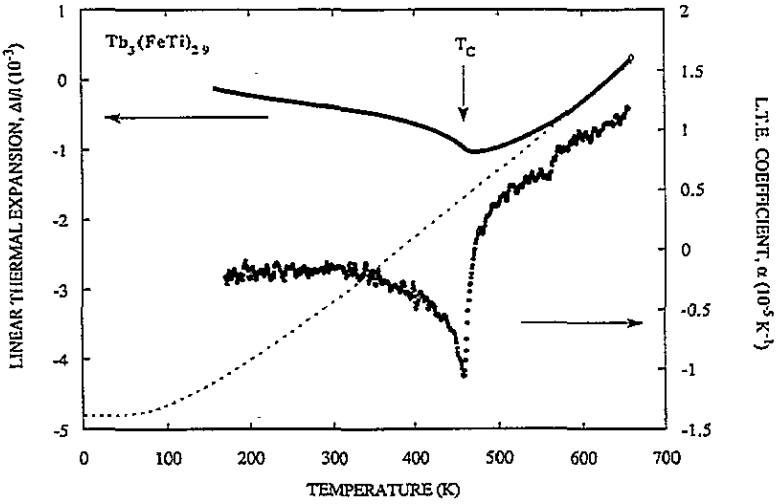

Figure 2. Linear thermal expansion (LTE) and thermal dependence of the LTE coefficient, α, of $Tb_3(Fe_{0.96}Ti_{0.04})_{29}$. The dashed line represents the calculated non-magnetic anharmonic phonon contribution.

Magnetic ordering and anisotropy. Measurements of the AC initial magnetic susceptibility, χ_{AC}, and magnetization in the temperature range 4–500 K showed an ordering temperature $T_c \simeq 455$ K and also a decrease of the saturation magnetization with temperature below room temperature as can be expected from a ferrimagnetic ordering (antiferromagnetic coupling between Fe and Tb magnetic sublattices). The thermal dependence of χ_{AC} is represented in figure 3. The behaviour shows a usual Hopkinson decrease with a change in the slope at $T \simeq 250$ K and the presence of a shoulder at $T \simeq 150$ K, which also was observed in $Nd_3(FeTi)_{29}$ [7]. At this temperature strong relaxation processes were observed during the χ_{AC} measurement process. The measurements, at 4 K and 300 K, of the polar dependence of the magnetization at 4 K and 300 K on aligned powder samples together with the results of SPD measurements indicate that the easy magnetization direction (EMD) lies along the same direction in the considered temperature range.

The magnetic anisotropy has been characterized by using the SPD technique [12]. It is worth recalling that in the SPD technique, the anisotropy field is measured through the observation of the singular point (saturation) which exists in the $M(H)$ curve along a magnetically hard direction. Following the SPD theory, this can be carried out directly on polycrystalline samples, by performing the successive derivatives d^nM/dH^n which are then plotted versus H. It has been shown that the minimum order of derivative n at which the discontinuity becomes apparent, in a random polycrystal, depends upon the symmetry

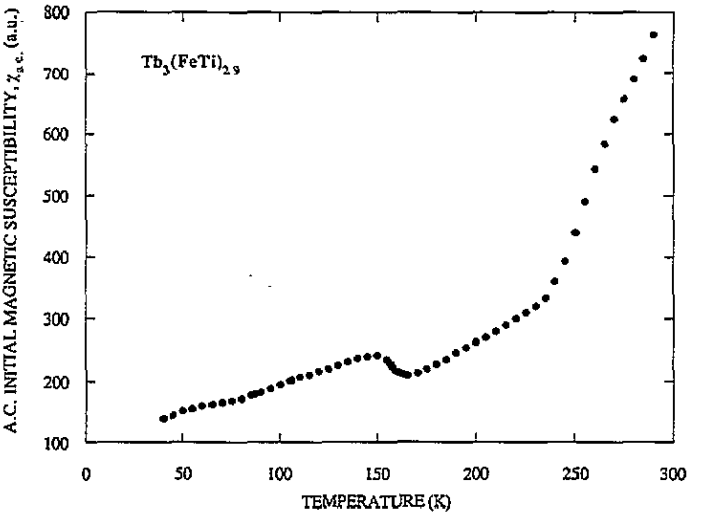

Figure 3. Thermal dependence of the AC initial magnetic susceptibility of $Tb_3(Fe_{0.96}Ti_{0.04})_{29}$.

(multiplicity) of the magnetically hard axis. The SPD theory, developed for uniaxial, cubic and trigonal systems, was not extended to monoclinic symmetry, for which a description of the anisotropy in terms of anisotropy constants has not been made to date. Thus, the application of the SPD method to a monoclinic structure is an empirical extrapolation, because there is no information on the directions which are extrema for the anisotropy energy and the minimum order of derivative which is required in order to evidence the discontinuity is unknown. In spite of that, by analogy with other symmetries, the three crystallographic axes could be assumed to be the extrema (easy and hard magnetization directions) for the anisotropy energy. In this instance it can be observed that the symmetry of the hard direction (which is a single axis) is similar to that of a uniaxial system having a hard axis (easy plane) with anisotropy in the basal plane. As a consequence, applying SPD techniques to a monoclinic three-axis system (one easy and two hard axes) two distinct peaks should be detected, corresponding to the anisotropy field along the two hard directions. The order of the derivative is expected to be $n = 3$ as in the case of an easy-plane system.

The experimental observations confirmed this hypothesis. Two peaks have been detected in the d^2M/dH^3. The intensity of these peaks has been alternatively enhanced by performing a suitable orientation (either in rotating or fixed-field systems) of the powdered specimens. The thermal dependence of the two measured anisotropy fields is reported in figure 4. The shape of the peak corresponding to the highest anisotropy field changes with decreasing temperature and, below 200 K, it is typical of a discontinuous approach to saturation as in the case of the type A1 FOMP in uniaxial systems.

From these macroscopic data we have no indications for the determination of the EMD at room temperature. On the other hand, the a axis has been reported to be the EMD at room temperature for the isostructural $Nd_3(FeTi)_{29}$ compound [6]. Furthermore, in this monoclinic cell, there is a distinct layering perpendicular to the b axis with layers containing only Fe or Fe and R atoms with a hexagonal coordination in the layers containing Fe.

By taking into account that the Fe anisotropy is dominant at high temperature and that Nd and Tb have the same sign of the second-order Stevens coefficient α_J, it can be expected that also in $Tb_3(FeTi)_{29}$ the EMD lies along the a axis at room temperature (or the c axis which are both parallel to the atomic layers). The anisotropy has to be different at low

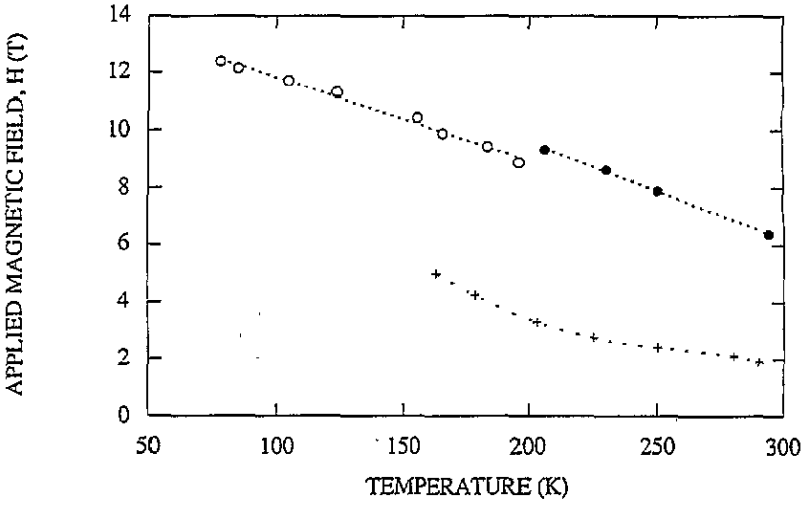

Figure 4. Thermal dependence of the anisotropy fields H_A (●, +) and critical field, H_{cr} (○) as determined from SPD measurements.

temperature because, differently from Nd, in the Tb compound no SRT has been found down to 4.2 K. In this instance the anisotropy fields observed can be tentatively considered as the field required to saturate M_s along the b axis, that is perpendicular to the layering (this should be the larger anisotropy field of 6.4 T at 293 K), while that of 1.9 T should be the field needed to rotate M_s in the plane parallel to the layering, from the a to the c axis (or vice versa). We should also mention that the relaxation mechanism observed in χ_{AC} at $T \simeq 150$ K in this compound, and also that observed in $Nd_3(FeTi)_{29}$ at the same temperature, cannot be related to the intrinsic interplay of the different anisotropic contributions which, in the presence of an applied field, originate the FOMP transition below 200 K. Some other extrinsic mechanism as reported for the $R_2Fe_{14}B$ [13] compounds has to be present.

We conclude: (i) We have obtained and characterized $Tb_3(FeTi)_{29}$. As far as we know, this is the first time that the existence of this compound has been reported. (ii) The crystallographic structure has been solved by a Rietveld refinement of the powder x-ray diffraction pattern, being isomorphous to $R_3(FeTi)_{29}$ for light rare earths, i.e. the monoclinic $P2_1/c$ space group. (iii) A large magnetovolume effect was observed in the LTE, pointing out a large volume effect on T_c. From these results, the insertion of interstitial atoms would significantly increase the ordering temperature. (iv) Two anisotropy fields are observed at 6.4 T and 1.9 T at room temperature; both increase with decreasing temperature. The a axis, as in $Nd_3(FeTi)_{29}$ at 293 K, seems to be the EMD in the entire range of temperature. (v) A first-order magnetization process takes place below 200 K.

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