Study of the crystal electric field interaction in $RFe_{11}Ti$ single crystals

# Study of the crystal electric field interaction in RFe$_{11}$Ti single crystals

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**Abstract.** Magnetization measurements along the main symmetry directions of the tetragonal structure, [100], [110] and [001], have been performed on several RFe$_{11}$Ti single crystals (R=Y, Tb and Ho), at applied high magnetic fields up to 12 Tesla and temperatures ranging from 4.2 to 300 K. From the measurements on the yttrium compound the second- and fourth-order anisotropy constants and the spontaneous magnetization of the Fe sublattice have been determined. The complex magnetic behaviour has been explained using a single-ion model for the crystal electric field (CEF) interaction and a mean-field model for the exchange interaction. A reliable set of CEF parameters and mean exchange field have been obtained for the TbFe$_{11}$Ti and HoFe$_{11}$Ti intermetallic compounds. All the experimental features observed, the first-order magnetization process under magnetic field in HoFe$_{11}$Ti and spin reorientation transition (SRT) in TbFe$_{11}$Ti, have been explained using such CEF and exchange parameters. A study of the character of the SRT observed in the TbFe$_{11}$Ti intermetallic compound has been undertaken by measuring the parallel and perpendicular components of the magnetization to the applied magnetic field. The experimental results obtained have been explained considering the coexistence of two magnetic phases for temperatures close to the spin reorientation one.

## 1. Introduction

The RFe$_{12-x}$M$_x$ (with R = rare earth and M = Mo, Ti, Si, V, W or Cr) intermetallic compounds crystallize in the tetragonal ThMn$_{12}$ structure (space group $I4/mmm$) and have been studied in depth during recent years in view of their interest as potential basis compounds for permanent magnet materials (see, for instance, [1] for a review of their magnetic properties). Although their performances do not reach those of other materials such as the Nd–Fe–B compounds, the crystallographic structure presents only one high-symmetry ($4/mmm$) site for the rare-earth ion, making these intermetallics excellent systems to study the crystal electric field and 3d–4f exchange interactions.

The magnetic structure has been explained considering the existence of two magnetic sublattices, Fe and rare earth, either ferromagnetically or ferrimagnetically coupled through the 3d–4f exchange interaction. Some compounds show up a spin reorientation transition (SRT), originated by the strong dependence on temperature of the magnetic anisotropy of the

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rare earth ion, combined with an iron sublattice anisotropy of opposite sign. The former can be described with a single-ion model involving quantities such as a mean exchange 3d–4f field and several crystal electric field (CEF) parameters according to the point symmetry of the rare earth site. The Fe sublattice anisotropy is assumed to be of 'easy-axis' type as in the YFe$_{11}$Ti compound [2, 3].

The sign of the second-order CEF gradient favours a contribution to uniaxial anisotropy for the R ions with second-order Stevens coefficient $\alpha_J > 0$ (i.e. R = Sm, Er, Tm and Yb), therefore an SRT could be expected for the compounds with $\alpha_J < 0$ (R = Nd, Tb, Dy and Ho). However, this SRT cannot be simply understood considering only the contribution of the second-order CEF term to describe the R magnetocrystalline anisotropy. For instance, the ErFe$_{11}$Ti compound shows an SRT at $T_{SR} \approx 60$ K from the $c$ axis to a non-collinear magnetic structure at low temperatures [3–5], in spite of the Fe and second-order R CEF contributions which favour the $c$ axis as easy magnetization direction in the entire range of temperatures. This fact may be considered as an indication of the relevance of high-order CEF terms to drive the SRT in these intermetallic compounds.

Among the 1:12 compounds the magnetic properties of the RFe$_{11}$Ti have been most intensively investigated [3, 5–7]. Several sets of CEF and exchange parameters have been obtained for all the compounds of the series [3, 5, 7] but all of them have been determined from magnetic measurements on polycrystalline samples and very different sets of values have been reported by the different authors (see, for instance, table 1 in [7]). Only in DyFe$_{11}$Ti has a relevant set of crystal electric field parameters been obtained by performing magnetization measurements along the main symmetry directions on a single crystal [8].

In the present paper we will focus our study on some RFe$_{11}$Ti single crystals (R = Y,Tb and Ho). The magnetic properties of the yttrium compound are supposed to represent the magnetic behaviour of the iron sublattice because the Y$^{3+}$ is a non-magnetic ion. The second-order anisotropy constant had been obtained from measurements of the anisotropy field on powder oriented samples [3]. In this paper we will determine second- ($K_1(T)$) and fourth-order ($K_2(T)$) anisotropy constants from magnetization measurements along the hard direction on a single crystal.

In the HoFe$_{11}$Ti compound several authors have pointed out the existence of a spin reorientation transition for temperatures around 50 K [4, 6]. However, others suggested that the easy magnetization direction remains along the $c$ axis in the whole temperature range [3, 5, 9]. Recent experimental results on initial susceptibility [5] and our measurements on single crystals confirm the latter view. A first-order magnetization process (FOMP) has also been reported at low temperatures [5, 9] at moderate applied magnetic field ($\approx 3$ T).

Very large discrepancies do exist with regard to the spin reorientation transition in the TbFe$_{11}$Ti compound (see [10] for a summary). Those different results have been ascribed to the fact that the temperature and character of the SRT are very sensitive to the applied magnetic field. Magnetization and torque measurements performed on single crystals [10–12] have confirmed the first-order character (discontinuous jump of the magnetization) of the SRT between the easy magnetization direction (EMD) at $T > T_{SR}$ ([001]) and the EMD at $T < T_{SR}$ ([100]). A spin reorientation transition temperature ($T_{SR}$) of about 325 K has been determined from such experiments [10, 11].

In order to gain insight into the main interactions existing in these compounds, the aim of the present work is to determine the CEF parameters and mean exchange field on the HoFe$_{11}$Ti and TbFe$_{11}$Ti compounds from magnetization measurements on single crystals. The character of the SRT transition of the TbFe$_{11}$Ti intermetallic will be studied by measuring the isothermal polar dependence of the parallel and perpendicular components of the magnetization to the applied magnetic field [13, 14].

## 2. Experimental details

All the experimental magnetization data reported in this work have been obtained from measurements on single-crystalline samples grown and cut in spherical shape at the Institute of Physics and Applied Mathematics (Ural State University, Ekaterinburg, Russia). Details of the preparation and quality of the single crystals have already been reported [9, 10, 12]. Magnetization measurements have been performed, with the magnetic field applied along the three main symmetry directions [100], [110] and [001], at several selected temperatures from 4.2 to 300 K. A sensitive vibrating sample magnetometer has been used in steady magnetic fields up to 12 T, produced with a superconducting coil. All the magnetic fields were corrected for the demagnetizing field using the demagnetizing factor obtained from the initial slopes of the magnetization curves along the easy direction.

Measurements of the magnetization components parallel ($M_\parallel$) and perpendicular ($M_\perp$) to the applied magnetic field were performed using an extraction magnetometer [13, 14] within the temperature range 200–340 K and applied magnetic fields of 0.2 and 0.5 T. The parallel magnetization component has a maximum when the magnetic field is applied along the EMD and a minimum when it is applied along the hard direction. $M_\perp$ has a zero value at both directions. From these measurements, it was possible to determine the EMD as a function of temperature and field with high accuracy.

## 3. Model description

In the R–M compounds, where M is a 3d transition metal, the magnetic behaviour is described as arising from two main contributions: one is given by the localized 4f electrons and the other by the itinerant magnetic electrons. The former contribution is well explained within the single-ion crystal electric field model. The complexity in the magnetic interaction introduced by the itinerant character of the 3d electrons is avoided by assuming that the magnetic behaviour of the 3d sublattice is similar to that observed in the non-magnetic 'rare earth' based compound Y–M. For this reason a careful study of the magnetic behaviour of the YFe$_{11}$Ti compound has been undertaken as a first step.

The exchange interaction between the rare earth and the iron sublattices is considered within the mean-field approximation. In the model we assumed the R–R exchange interaction to be negligible in relation to the R–M interaction. The M–M (3d–3d) interaction is by far the strongest and determines the magnetic ordering temperatures, coupling ferromagnetically the iron magnetic moments, but it gives an irrelevant contibution to the study of the magnetocrystalline anisotropy, because it just introduces an isotropic reference level or a self-energy term.

### 3.1. Iron sublattice contribution: YFe$_{11}$Ti compound

The magnetic behaviour of the iron sublattice is characterized by measuring the thermal dependencies of the spontaneous magnetization, $M_{Fe}(T)$, and the magnetic anisotropy constants. This is phenomenologically described by the second- and fourth-order anisotropy constants, $K_1$ and $K_2$ respectively. In order to determine the values of $M_{Fe}(T)$, $K_1(T)$ and $K_2(T)$, magnetization measurements have been performed along the easy magnetization direction (EMD), [001], and the hard magnetization direction (HMD), [100]. The magnetization isotherms for some selected temperatures are shown in figure 1, for the field applied along the EMD and HMD. From the magnetization measurements along the EMD, $M_{Fe}(T)$ has been obtained in the temperature range 4.2 to 300 K (see figure 2). The

value obtained at 4.2 K, $M_{Fe} = 19.4 \pm 0.1$ $\mu_B$/fu, closely agrees with previously reported values [3, 10]. A negligible anisotropy in the value of the 3d saturation magnetization has been observed between the EMD and HMD (see figure 1).
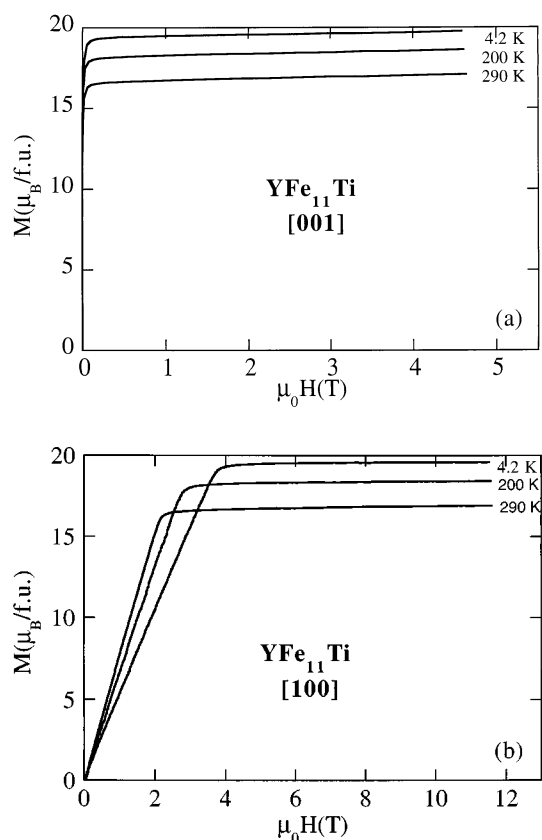


**Figure 1.** Magnetization isotherms at some selected temperatures for the YFe$_{11}$Ti single crystal (a) along the easy magnetization direction [001] and (b) along the hard magnetization direction [100].

The anisotropy constants have been determined from the magnetization isotherms along the hard direction [100] (see figure 1(b)). $K_1(T)$ and $K_2(T)$ have been obtained using the Sucksmith–Thompson relation for an easy-axis system [15]

$$\frac{H}{M_a} = \frac{2K_1}{M_s^2} + \frac{4K_2}{M_s^4} M_a^2 \tag{1}$$

where $H$ and $M_a$ respectively are the *internal* magnetic field and the magnetization along the HMD, and $M_s$ the spontaneous magnetization. By plotting $H/M_a$ against $M_a^2$, at the different experimental temperatures, we have obtained the values of $K_1(T)$ and $K_2(T)$ as shown in figure 3.

The values for the anisotropy constants at 4.2 K for YFe$_{11}$Ti, according to our experimental results, are: $K_1 = 24 \pm 0.2$ K fu$^{-1}$ and $K_2 = 0.44 \pm 0.2$ K fu$^{-1}$. The value previously reported at 4.2 K by Hu *et al* [3] is 25 K fu$^{-1}$ at 4.2 K. Such a discrepancy can be explained considering that the value of $K_1$ obtained in [3] has been derived from
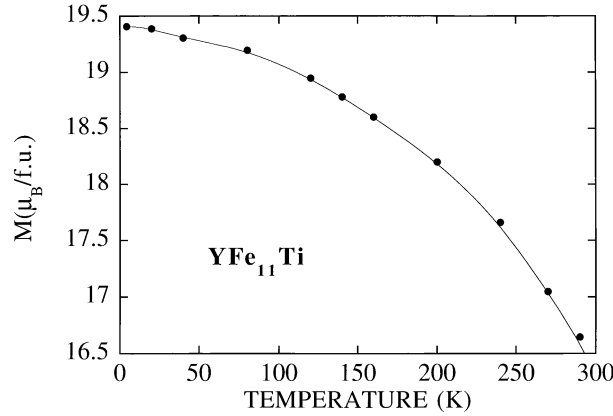
**Figure 2.** Spontaneous magnetization of the YFe$_{11}$Ti intermetallic compound as a function of temperature (the line is a visual guide).

the anisotropy field determined in a polycrystalline sample. According to (1) the anisotropy field (then $M_a = M_s$) is given by $H_a = (2K_1 + 4K_2)/M_s$. In the previous determination of the second-order anisotropy constant [3] the fourth-order one was neglected. Therefore, Hu *et al* [3] assumed $K_1 = (1/2)H_aM_s$. But, if the fourth-order anisotropy constant $K_2$ is not neglected, we have that $K_1 + 2K_2 = (1/2)H_aM_s$. Therefore, if we compare the previous value of $K_1 = 25$ K fu$^{-1}$ with our value of $K_1 + 2K_2 = 24.9 \pm 0.4$ K fu$^{-1}$ the agreement is very good.

### 3.2. Rare earth sublattice: crystal electric field and 4f–3d exchange interactions

In the presence of an internal magnetic field $\boldsymbol{H}_i$, the Hamiltonian describing the magnetic properties of the R$^{3+}$ ions in the tetragonal RFe$_{11}$Ti compounds can be written as

$$H = H_{CEF} + 2(g_J - 1)\mu_B \boldsymbol{J} \cdot \boldsymbol{H}_{ex}(T) + g_J \mu_B \boldsymbol{J} \cdot \boldsymbol{H}_i \qquad (2)$$

where $H_{CEF}$ represents the CEF interaction on the rare earth site, which, in tetragonal symmetry and considering only the ground state multiplet $|L, S, J, M_J\rangle$ of the R$^{3+}$ ion, can be expressed as

$$H_{CEF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 \qquad (3)$$

where the $B_n^m$ are the CEF parameters and the $O_n^m$ are the CEF Stevens operators. The second term of equation (2) represents the 3d–4f exchange interaction, which can be expressed, within the mean-field approximation, by an effective exchange magnetic field $\boldsymbol{H}_{ex}(T)$, considered proportional and antiparallel to the iron sublattice magnetization ($\boldsymbol{H}_{ex}(T) = \boldsymbol{H}_{ex}(0)(M_{Fe}(T)/M_{Fe}(0))$). $\boldsymbol{J}$ is the R$^{3+}$ total angular momentum and $g_J$ the Landé factor. The last term of equation (1) describes the Zeeman interaction of the R$^{3+}$ sublattice under an internal field $\boldsymbol{H}_i$.

The magnetic free energy of the R$^{3+}$ sublattice is obtained from the canonical partition function $Z = \sum_n \exp(-E_n/k_B T)$ where $E_n$ are the eigenvalues of the Hamiltonian given by expression (2). The free energy of the rare earth sublattice is given by,

$$F^R(\theta, \varphi, \theta_H, \varphi_H, H_i, T) = -k_B T \ln Z \qquad (4)$$
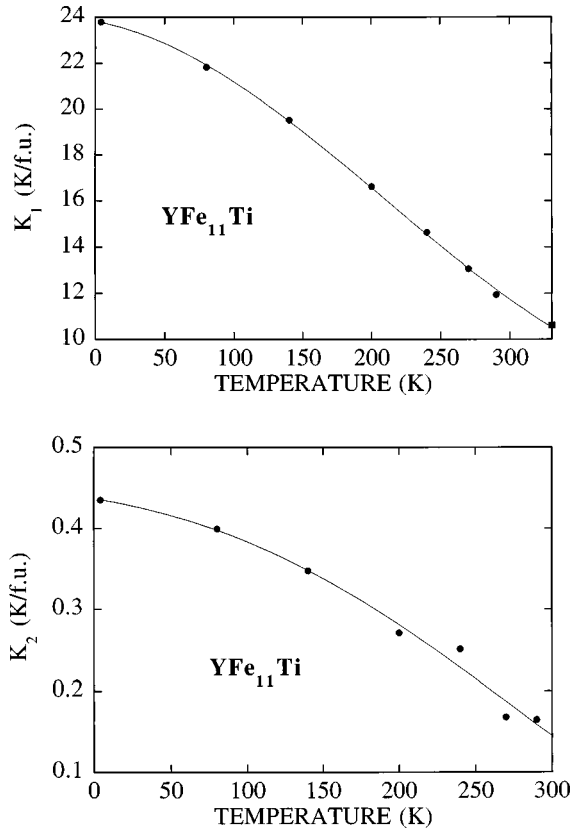
**Figure 3.** Thermal dependence of the second-order $(K_1(T))$ and fourth-order $(K_2(T))$ magnetocrystalline anisotropy constants of the $YFe_{11}Ti$ compound obtained according to the Sucksmith–Thompson relation (1) (●) (the lines are a visual guide). The value of $K_1$ at 328 K (■) has been determined from the spin reorientation transition temperature of the $TbFe_{11}Ti$ compound (see text for details).

where $H_i$ is the magnitude of the internal field, $\theta_H$ and $\varphi_H$ are the standard spherical angles determining the direction of $H_i$ and $\theta$ and $\varphi$ are the same angles for the exchange mean-field, $H_{ex}$, direction.

### 3.3. Crystal electric field parameter determination method

The total free energy is calculated by adding to $F^R$ the uniaxial Fe sublattice anisotropy free energy together with the Zeeman interaction for the Fe sublattice, i.e.

$$F(\theta, \varphi, \theta_H, \varphi_H, H_i, T) = F^R(\theta, \varphi, \theta_H, \varphi_H, H_i, T) + K_1(T)\sin^2\theta + K_2(T)\sin^4\theta$$
$$- M_{Fe}(T)H_i[\sin\theta\sin\theta_H\cos(\varphi_H - \varphi) + \cos\theta\cos\theta_H] \qquad (5)$$

where $M_{Fe}(T)$, $K_1(T)$ and $K_2(T)$ respectively are the magnetization and the anisotropy constants of the Fe sublattice, taken as for the $YFe_{11}Ti$ compound, scaled to the Curie temperature of the corresponding $RFe_{11}Ti$ compound. The magnetic structure at any given temperature and applied magnetic field is determined by the exchange mean-field equilibrium angles, $\theta_0$ and $\varphi_0$, which minimize the total free energy given by expression (5).

The magnetic moment components of the $R^{3+}$ ion, within the intermetallic crystalline lattice, is then calculated from the expression

$$m_i - \frac{g_J \mu_B}{Z} \sum_n \langle n|J_i|n\rangle \exp\left(\frac{-E_n}{k_B T}\right) \qquad (i = x, y, z) \qquad (6)$$

where $E_n$ are the energy eigenvalues and $|n\rangle = \sum a_{nJ}|JM_J\rangle$ the wavefunction eigenvectors of the rare earth Hamiltonian (1) for the equilibrium angles $\theta_0$ and $\varphi_0$. The magnetization of the RFe₁₁Ti compound is the addition of the contributions from the R and Fe sublattices

$$\mathbf{M}(T) = \mathbf{m}(T) + \mathbf{M}_{Fe}(T, \theta_0, \varphi_0). \qquad (7)$$

To determine the sets of $\{B_n^m, H_{ex}(0)\}$ parameters giving an appropriate description of the magnetic properties reported in this paper, a random search over the six-dimensional parameter space has been done. Several thousand parameter sets have been analysed. A $\{B_n^m, H_{ex}(0)\}$ set is chosen randomly within a certain range in the parameter space. Using the procedure described above, the magnetization $M(T)$, given by equation (7), is calculated and compared with the experimental values. As described in previous works [16, 17] such a process is made step by step as follows. Firstly, an experimental magnetic isotherm measured at temperature $T_1$, $M_{exp}(T_1)$, is considered. If for a parameter set the calculated magnetization $M(T_1)$ lies for all the field range within the experimental error, this set is considered for further analysis. The number of sets is reduced step by step by imposing a satisfactory fit of the magnetization isotherms measured at different temperatures $T_2, T_3, \ldots$. This process continues until the best fit is reached for all the measured isotherms, obtaining in this way the final set of CEF and exchange field parameters.

## 4. Results and discussion

### 4.1. HoFe₁₁Ti compound

The isotherms obtained from the magnetization measurements at some selected temperatures are shown in figure 4. In all the temperature range studied, the easy magnetization direction corresponds to the [001] axis. Such a result confirms the absence of a spin reorientation transition in this compound. A first-order magnetization process (FOMP) is observed at temperatures lower than 120 K. As the saturation is not reached after the magnetization 'jump', the FOMP observed in this compound can be classified as corresponding to type II, confirming the results obtained in [5] using the singular-point detection (SPD) technique in polycrystalline samples. As in the FOMP in the DyFe₁₁Ti single crystal [8] a continuous increase of the magnetization instead of a jump is observed for magnetic fields around the critical magnetic field ($H_{CR}$) [8]. Following the model developed for the DyFe₁₁Ti compound [18] this continuous variation of the magnetization can be ascribed to the coexistence of a low-field (LF) conical phase 1 (CP1) with angle $\theta_1 \approx 7°$ and high-field (HF) conical phase 2 (CP2) with angle $\theta_2 \approx 60°$ for magnetic fields around $H_{CR}$ (at $T = 4.2$ K), with relative phase volumes depending on the applied magnetic field. The presence of the two phases in the sample can be related to the existence of two minima in the total free energy at $\theta_1 = 0°$ and $\theta_2 \approx 60°$, as theoretically predicted at 4.2 K for an applied magnetic field of 0 T [8]. The applied magnetic field favours the growing of the HF CP2 phase [18].

The set of exchange field ($H_{ex}(0)$) and CEF gradient coefficients, $A_n^m$, where $A_n^m = B_n^m/\theta_n\langle r_n\rangle$ ($\theta_n$ are the Stevens coefficients [19] and $\langle r^n\rangle$ are the Hartree–Fock radial integrals [20]), used to explain the experimental magnetization isotherms are shown in table 1. The random search of the CEF parameters has been done in a broad region of
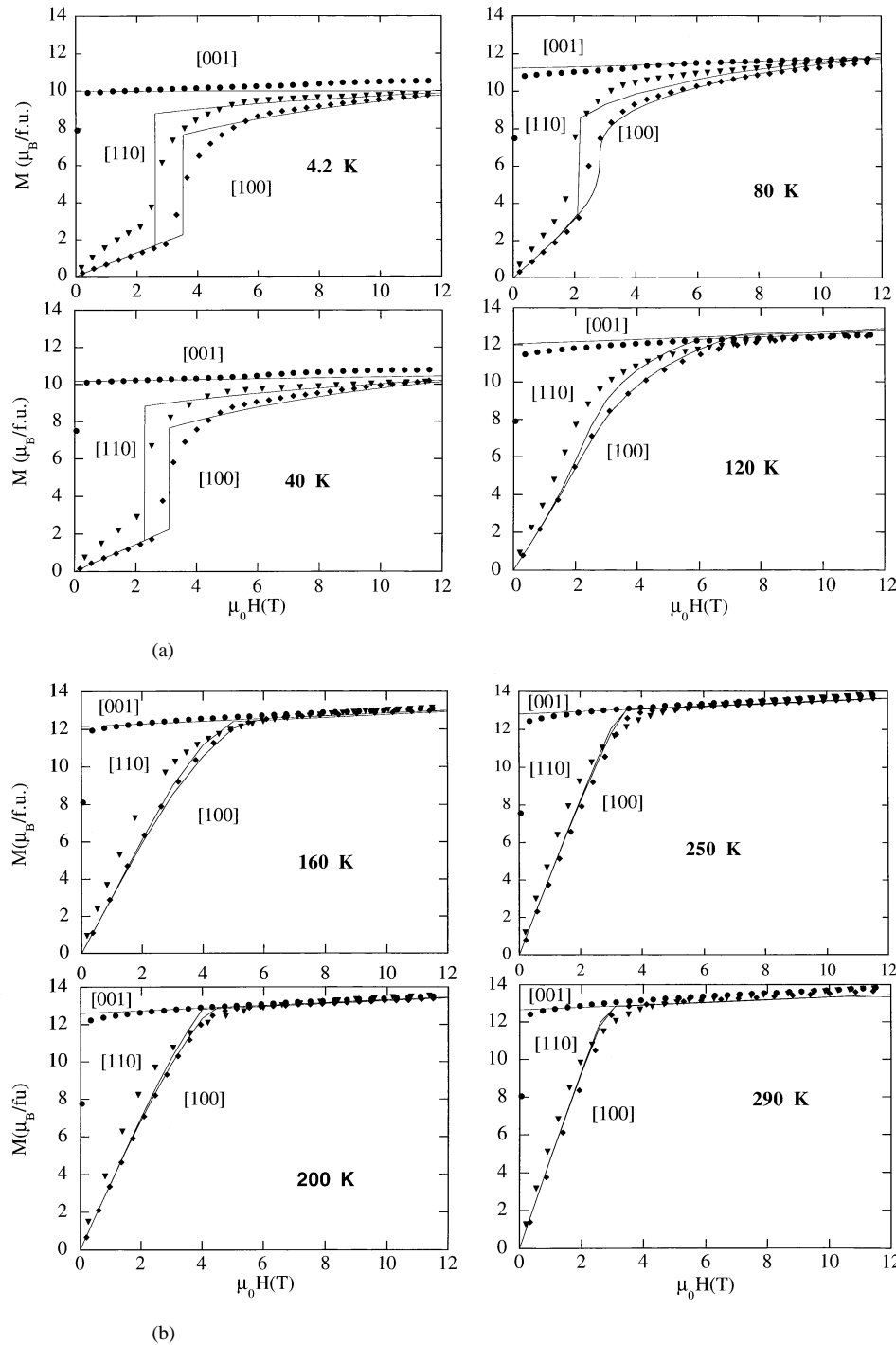
**Figure 4.** Magnetization isotherms for the HoFe$_{11}$Ti single crystal, for the magnetic field applied along the high-symmetry directions at several selected temperatures: (a) $T = 4.2$ K, 40 K, 80 K and 120 K, (b) $T = 160$ K, 200 K, 250 K and 290 K. The solid symbols represent the experimental values and the lines the model fit for the set of CEF and exchange field parameters determined in this work (see table 1).

the $\{B_n^m, H_{ex}(0)\}$ space including the scaled parameters for the HoFe$_{11}$Ti compound as obtained from those reported for the DyFe$_{11}$Ti compound [8]. A good agreement has been obtained, giving a satisfactory description of all the magnetization processes observed within the whole temperature range studied (see figure 4). A small increase of the iron sublattice magnetization in YFe$_{11}$Ti ($\approx 3\%$) has been introduced for $M_{Fe}(T)$ to improve the theoretical fit. This increase was also introduced in the analysis of magnetization isotherms on a DyFe$_{11}$Ti single crystal [8], and it is in good agreement with the results of the Mössbauer effect in the RFe$_{11}$Ti series [21]. Such a behaviour has been also observed in the R$_2$Fe$_{14}$B [22] and R$_2$Fe$_{17}$ [17] intermetallic compounds and can be ascribed to the enhancement of the exchange mean field, produced by the presence of the R magnetic moment on the 3d moments [17].

The CEF coefficients, $A_n^m$, obtained in the present work have close values to the ones determined from the magnetization analysis on the DyFe$_{11}$Ti single crystal (see table 1). The discrepancies observed may originate from the different values taken for Fe sublattice anisotropy constants. The exchange field relation is $H_{ex}(\text{HoFe}_{11}\text{Ti}) \approx 0.83 H_{ex}(\text{DyFe}_{11}\text{Ti})$, and a similar reduction was also found in the R$_2$Fe$_{14}$B compounds [23]. At low temperatures it has not been possible to explain the magnetic anisotropy within the basal plane of the tetragonal structure at magnetic fields lower that the critical value. Such a theoretical behaviour has been also found by Kou *et al* [5] even using CEF coefficients and exchange field quite different from those reported in this paper ($A_2^0 = -28.2$, $A_4^0 = -3.2$, $A_4^4 = -30.3$, $A_6^0 = 1.2$, $A_6^4 = 0$ and $H_{ex}(0) = 155$ K). The critical fields obtained in [5] ($H_{CR}[100] = 3.2$ T, $H_{CR}[110] = 2.4$ T [24]) are quite similar to the ones obtained with our CEF and $H_{ex}(0)$ parameters ($H_{CR}[100] = 3.5$ T, $H_{CR}[110] = 2.6$ T). Such a result is not surprising because, as it has been shown, it is possible to find a large region within the $\{B_n^m, H_{ex}(0)\}$ parameter space giving a good fit to experiment at only one temperature [16, 17]. A dramatic reduction of such a region is produced by introducing more restrictions such as the fitting of the single-crystal magnetization isotherms within a wide range of temperatures, which is our situation.

**Table 1.** Crystal electric field coefficients, $A_n^m$ (in K $a_0^{-n}$ units), and exchange field, $\mu_B H_{ex}$, (in K units), at 0 K obtained from the fitting of the single-crystal magnetization isotherms. The data of the DyFe$_{11}$Ti compound have been reported in [8]. $A_n^m = B_n^m / \theta_n \langle r^n \rangle$, where $B_n^m$ are the CEF parameters, $\theta_n$ represent the Stevens coefficients and $\langle r^n \rangle$ are the Hartree–Fock radial integrals.

| RFe$_{11}$Ti | $A_2^0$ | $A_4^0$ | $A_4^4$ | $A_6^0$ | $A_6^4$ | $\mu_B H_{ex}(0)$ |
|---|---|---|---|---|---|---|
| TbFe$_{11}$Ti | $-52.5$ | $-0.27$ | $-0.87 \times 10^{-2}$ | $0.21 \times 10^{-1}$ | $-8.9$ | 126 |
| DyFe$_{11}$Ti | $-32.3$ | $-12.4$ | $-118$ | $2.56$ | $-0.64$ | 121 |
| HoFe$_{11}$Ti | $-20.5$ | $-11.1$ | $-153.2$ | $5.02$ | $-0.81$ | 100 |

## 4.2. TbFe$_{11}$Ti compound

The experimental isotherms for the TbFe$_{11}$Ti compound are shown in figure 5, at some selected temperatures. The EMD lies along the [100] axis within the studied temperature range of 4.2–300 K. The magnetic anisotropy within the (001) plane is very large and, in the whole temperature range studied, the magnetic field needed to saturate the magnetization along the [110] direction is bigger than the one needed to saturate along the [001] direction (see figure 5).
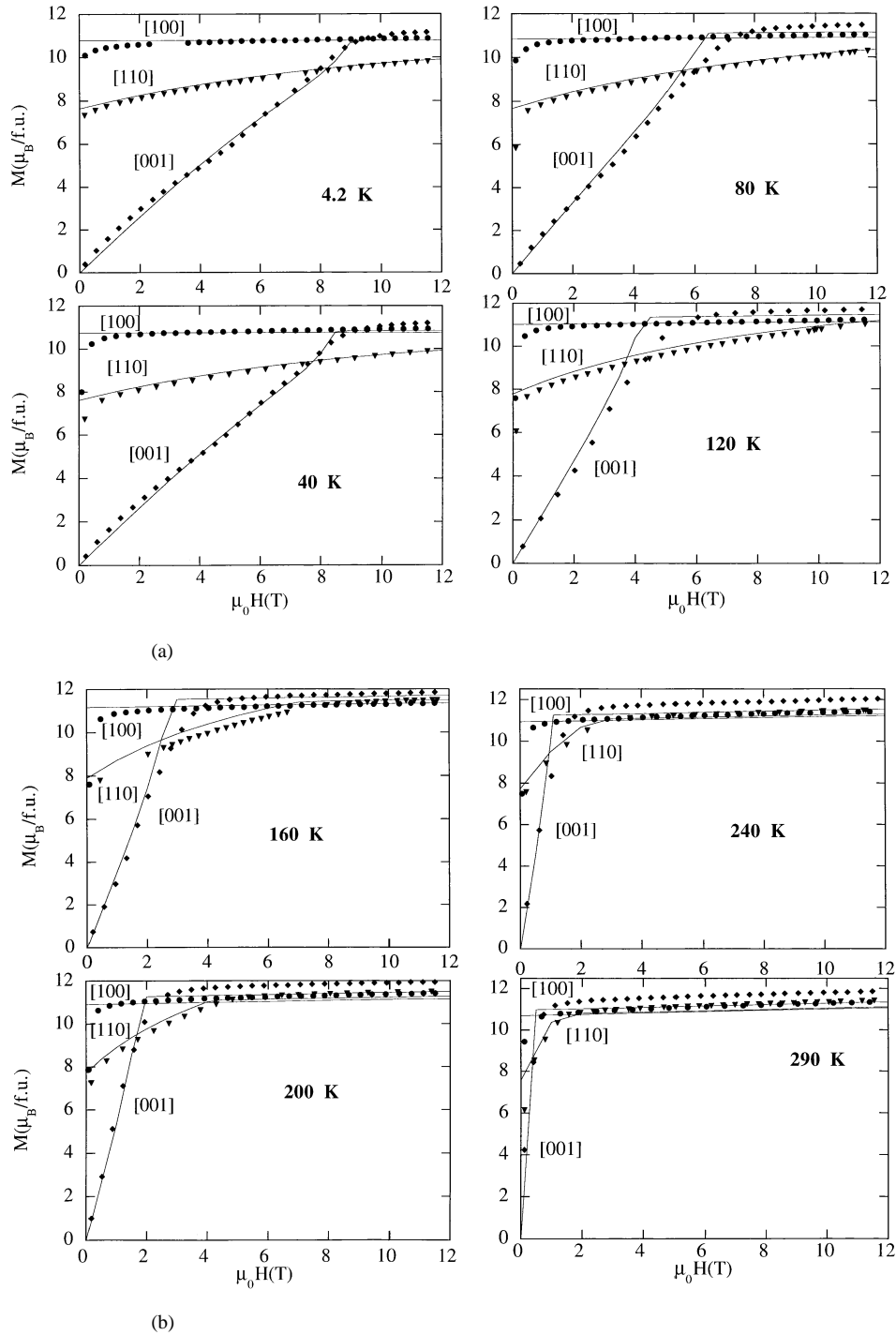
**Figure 5.** Magnetization isotherms for the TbFe$_{11}$Ti single crystal, for the magnetic field applied along the high-symmetry directions at several selected temperatures: (a) $T$ = 4.2 K, 40 K, 80 K and 120 K, (b) $T$ = 160 K, 200 K, 250 K and 290 K. The solid symbols represent the experimental values and the lines the model fit for the set of CEF and exchange field parameters determined in this work (see table 1).

Hu *et al* [8] have already pointed out that the CEF and exchange parameters determined for DyFe$_{11}$Ti, when scaled to the TbFe$_{11}$Ti compound, cannot explain the magnetic behaviour observed for this compound. In fact the scaled parameters give a spin reorientation transition at $T_{SR} \approx 130$ K, far from the experimentally observed at $T_{SR} \approx 325$ K. As it can be seen in figure 5, the CEF coefficients obtained from our random scan give a satisfactory explanation of the experimental magnetization isotherms, and, as expected, they are very different from the reported ones in [8], although $H_{ex}(0)$ is quite similar (see table 1). The origin of such a discrepancy is not clear yet. An anomalous value for $A_2^0$ has been also obtained for the Pr and Yb ions in the R$_2$Fe$_{14}$B series and it has been attributed to an incipient rare earth valence instability [25].
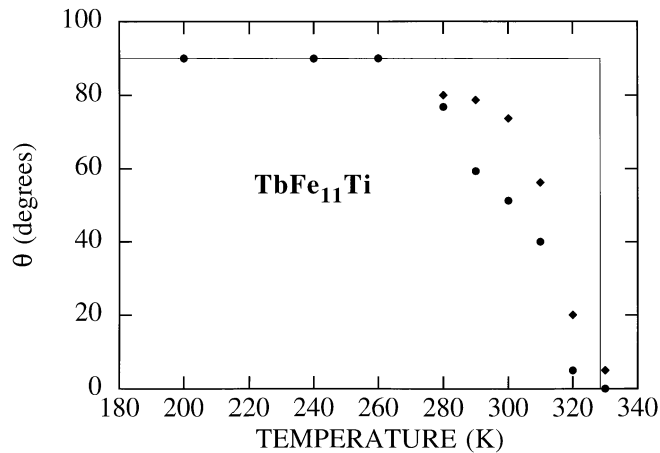


**Figure 6.** Temperature dependence of the spin reorientation angle, $\theta$, between the direction of $M$ and the $c$ axis. The symbols represent the experimental results obtained from the measurements of $M_\parallel$ and $M_\perp$ at 0.2 T ($\bullet$) and 0.5 T ($\blacklozenge$) for the TbFe$_{11}$Ti intermetallic compound. The line is the model calculation using the parameters of table 1 (see text for details).

The spin reorientation transition in this compound has been studied by performing measurements of the parallel and perpendicular components of the magnetization to the applied magnetic field in the temperature range 200–340 K. The experimental results are summarized in figure 6 for applied magnetic fields of 0.2 and 0.5 T, showing a continuous rotation of the macroscopic EMD between the easy-plane magnetic phase and easy-axis magnetic phase. The intermediate (between 0 and 90 degrees) $\theta$ angle depends on the magnetic applied field. This behaviour has been already observed for the low-temperature SRT in DyFe$_{11}$Ti [18, 26]. However, the predicted theoretical result, also shown in figure 6, using the CEF and exchange parameters reported in table 1, clearly predicts a first-order SRT. To explain such a discrepancy we can consider, as in the case of DyFe$_{11}$Ti [18], that in the temperature range 260–330 K the sample consists of two mixed magnetic phases corresponding to the low-temperature ($T < 260$ K) planar phase (PP) with $\theta = 90°$, and the high-temperature ($T > 330$ K) axial phase (AP) with $\theta = 0°$. In the intermediate-temperature region the two phases coexist, with different relative volumes depending on the temperature and the magnetic field. As a consequence, an average EMD, intermediate between the axial and planar structures, is observed for such a temperature region.

As already mentioned in the case of HoFe$_{11}$Ti, the existence of the two above-mentioned magnetic phases can be related to the existence of two minima for the total free energy. In
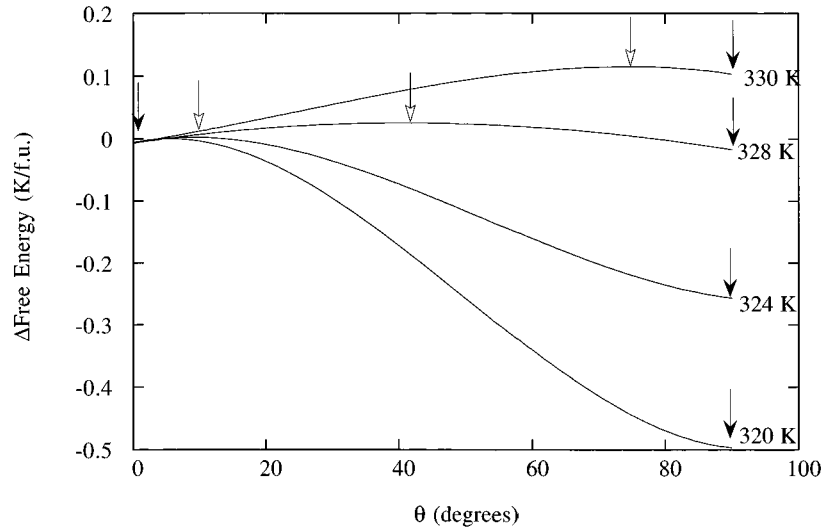
**Figure 7.** Model calculated magnetic free energy, within the (010) plane, at temperatures close to $T_{SR} \approx 328$ K for the TbFe$_{11}$Ti compound. The solid arrows shown the energy minima at $\theta = 0°$ and $\theta = 90°$ and the open arrows the intermediate maxima. For all the temperatures the free energy has been normalized by subtracting the free energy at $\theta = 0°$.

figure 7 we show the theoretical calculation of the free energy around $T_{SR} = 328$ K, where two close energy minima at $\theta = 90°$ (PP) and $\theta = 0°$ (AP), separated by a small shallow energy barrier, can be observed.

The values for the anisotropy constants of the Fe sublattice have only been obtained up to 290 K. As the SRT in the TbFe$_{11}$Ti compound takes place at $T_{SR} \approx 328$ K, the value of $K_1$ has been taken as a free parameter to select the SRT at $T_{SR} = 328$ K and $K_2$ has been neglected. The value of $K_1$ (at 328 K) obtained under this constraint shows a good agreement with that expected from the thermal evolution of $K_1(T)$, as obtained from the magnetization isotherms (see figure 3). Such an agreement gives further support to the validity of the CEF and exchange parameters obtained in this work.

## 5. Conclusions

The parameter space $\{B_n^m, H_{ex}(0)\}$, describing the CEF and 3d–4f exchange interaction in some RFe$_{11}$Ti intermetallic compounds (R = Tb and Ho), has been systematically analysed. A reliable set of CEF parameters and exchange field value have been found from the analysis of high-field magnetization measurements on single crystals for the HoFe$_{11}$Ti and TbFe$_{11}$Ti compounds. The parameters obtained describe quite accurately the magnetic behaviour experimentally observed, in particular the FOMP under field observed in the HoFe$_{11}$Ti compound and the spontaneous spin reorientation transition observed in the TbFe$_{11}$Ti compound. The character of first-order transitions observed in these compounds, FOMP (in HoFe$_{11}$Ti) and SRT (in TbFe$_{11}$Ti), have been discussed under the assumption of the existence of two magnetic phases that coexist in certain range of applied magnetic field and temperature respectively.

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