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A Mössbauer study of temperature-driven spin-reorientation transitions in $TbFeO_3$

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Abstract. Reorientations of Fe^{3+} spins have been studied in $TbFeO_3$ single-crystal absorbers by Mössbauer spectroscopy. At low temperature we observed two closely spaced changes of direction of the Fe^{3+} spins. Below 6.5 K the spins moved from the a towards the c orthorhombic axis with decreasing temperature. This movement was reversed at approximately 4.2 K and the movement back to the a axis was complete at 3.5 K. The maximum deviation from the a axis was about 55° and somewhat dependent on crystal stress. These rotations are attributed to the temperature dependence of the Fe–Tb and Tb–Tb interactions.

1. Introduction

The rare-earth orthoferrites $RFeO_3$ (R stands for a rare earth or Y) have the crystal structure of a distorted perovskite described by the D_{2h}^{16}–$Pbnm$ rhombic space group. At higher temperatures, the predominant interactions are between the Fe ions. The superexchange is by far the strongest. The Fe^{3+} magnetic moments order antiferromagnetically below T_N (681 K in the case of $TbFeO_3$) due to its symmetric part, while the anisotropic antisymmetric exchange (much weaker) causes a slight canting of the spins resulting in a weak (transverse) ferromagnetic moment. Dipolar interactions and single-ion anisotropy align the Fe^{3+} spins and the antiferromagnetic vector $\boldsymbol{G}$ (in the notation of Bertaut [1]) along the a rhombic axis, the weak ferromagnetic moment $\boldsymbol{F}$ being parallel to the c axis. The effect of the rare-earth ions on the Fe subsystem is negligible at higher temperatures, where the former can be described as a paramagnetic system in the crystal field produced by the latter. Using the same notation, this configuration is described as $\Gamma_4(G_xA_yF_z;\ f_z)$. Here Γ_4 is one of eight irreducible representations of the space group D_{2h}^{16}–$Pbnm$. G_i and F_i ($i = x, y, z,$) are the non-zero components of $\boldsymbol{G}$ and $\boldsymbol{F}$. $\boldsymbol{G}$, $\boldsymbol{F}$, $\boldsymbol{A}$ (and $\boldsymbol{C}$) are four vectors that form the basis of the irreducible representations Γ_i ($i = 1, 2, \ldots, 8$) and are defined as linear combinations of the four Fe^{3+} sublattice magnetizations as follows: $\boldsymbol{F} = \boldsymbol{M}_1 + \boldsymbol{M}_2 + \boldsymbol{M}_3 + \boldsymbol{M}_4$, $\boldsymbol{G} = \boldsymbol{M}_1 - \boldsymbol{M}_2 + \boldsymbol{M}_3 - \boldsymbol{M}_4$, $\boldsymbol{A} = \boldsymbol{M}_1 - \boldsymbol{M}_2 - \boldsymbol{M}_3 + \boldsymbol{M}_4$, $\boldsymbol{C} = \boldsymbol{M}_1 + \boldsymbol{M}_2 - \boldsymbol{M}_3 - \boldsymbol{M}_4$. Since $|\boldsymbol{G}| \gg |\boldsymbol{F}|$, $|\boldsymbol{A}|$ and $|\boldsymbol{C}|$ at temperatures well below T_N, we may assume that $\boldsymbol{G}$ is parallel to the Fe^{3+} magnetic moments or spins. Only three modes, Γ_1, Γ_2 and Γ_4, are allowed for the Fe sub-system by the crystal symmetry. Four analogous vectors $\boldsymbol{g}$, $\boldsymbol{f}$, $\boldsymbol{a}$ and $\boldsymbol{c}$ are defined as linear combinations of Tb^{3+} sublattice magnetizations [1].

As the crystal is cooled, the rare-earth ions become increasingly polarized. The temperature-dependent R–Fe interactions are manifest then in some orthoferrites by a

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continuous rotation of the vector of antiferromagnetism G towards the c axis. This is what has been reported also to take place in $TbFeO_3$ at about 6 K [2]. On further cooling the Tb^{3+} spins have been found by neutron diffraction to order antiferromagnetically at about 4 K in the $\Gamma_8(a_x g_y)$ mode. However, that mode is incompatible with those allowed for the Fe sub-system (Γ_1, Γ_2 and Γ_4). It has been assumed [3] that the Fe^{3+} spins should then return to their high-temperature configuration $\Gamma_4(G_x A_y F_z)$, i.e. along the a axis. However, there was some discrepancy between the neutron-diffraction and Mössbauer data in [3]. In the case of random powder absorbers, for instance, information about a Fe^{3+} spin rotation would be expected to come from the quadrupole shift 2ϵ in the nuclear Zeeman sextet. That parameter was reported by Bertaut *et al* [3] to vary only slightly and within the experimental errors, so the authors tried to explain such behaviour by a special orientation of the electric field gradient (EFG) principal axes. A Mössbauer experiment with a partially oriented $TbFeO_3$ powder absorber [4] provided some additional but still limited evidence of Fe spin rotations. Another study of $TbFeO_3$ by torque measurements [5] suggested that the weak ferromagnetic moment of the Fe sub-system vanished below 17 K, which usually implies Fe^{3+} spins in the $\Gamma_1(G_y)$ mode, i.e. along the b axis. A single-crystal magnetization study by Gordon *et al* [6] did not show any spin reorientation in $TbFeO_3$ at temperatures above 4.2 K. Now single-crystal Mössbauer spectroscopy offers the possibility of directly detecting a spin rotation through the relative line intensities of the ^{57}Fe nuclear Zeeman sextet. We therefore performed such experiments on single-crystal absorbers of $TbFeO_3$ in the interval 1.3–295 K. Our aim was to investigate the temperature-driven Fe^{3+} spin rotations at low temperatures, especially following observations of apparent Fe–R decoupling in $YbFeO_3$ in applied magnetic fields [7].

2. Experimental procedure

Two samples were prepared from a large $TbFeO_3$ single crystal of natural Fe composition, grown as described in [8]. One was cut as a (bc)-plane absorber (γ-quanta propagating along the a rhombic axis); the other was an (ab) cut. The slices were thinned down to $\sim$35 μm (about 6 mg cm^{-2} natural Fe) by abrasives and diamond paste. Both faces of each absorber were given a final polish with 0.3 μm diamond paste. The plates were then glued to 0.2 mm thick Be disks by an adhesive BF-2, which is known to retain some elasticity even at very low temperatures [9]. Finally, the orientations were checked by Laue diffraction and deviations from the respective rhombic planes were found to be less than 1°. The usable areas were 0.3–0.5 cm^2.

Two types of cryostat were used for the measurements. A continuous He gas-flow apparatus provided cooling down to 4.3 K in low-pressure He exchange gas. The temperature was stabilized within less than 0.1 K by an ITC-4 temperature controller. A bath cryostat was used for the 4.2–1.3 K interval by pumping the He tank, the sample being immersed in the liquid itself. The temperature stability was better than $\pm$0.002 K at about 3–4 K and $\pm$0.01 K at 1.3 K.

Mössbauer spectra were collected in standard transmission geometry in constant-acceleration double-ramp mode, using $^{57}Co(Rh)$ sources and $Ar(CH_4)$ proportional counters. The absorbers were always perpendicular to the γ-ray beam, with a small misalignment error of 3–4°. All parameters reported were obtained by least-squares fitting a single Zeeman sextet with Lorentzian lines to the experimental spectra.

3. Results and discussion

Some of the spectra obtained from the (*bc*) absorber are shown in figure 1. The fitted Mössbauer parameters from this absorber are plotted in figures 2 and 3. Figure 2 shows the temperature variation of the relative line intensities (RLIs) of the second and fifth ($\Delta m = 0$) lines in the ^{57}Fe nuclear Zeeman sextet, defined as a ratio of the respective line areas $R = (A_2 + A_5)/(A_3 + A_4)$. This parameter varies between zero when $^{57}Fe^{3+}$ ion spins are parallel to the γ-rays, and four when they are perpendicular. R provides direct evidence of the orientation of G with respect to the γ-ray beam and the absorber itself. As can be seen from the graph, this vector was parallel to the γ-rays, i.e. to the a rhombic axis, down to about 6 K. (The room-temperature value of R was also zero.) On further cooling G started rotating gradually towards (*bc*). The maximum angle Θ between the a axis and the ferric spins calculated from R without a thickness correction, $55° \pm 6°$, was reached at 4.2 K. Accounting for the finite thickness of the absorber would increase this value only slightly. (The error includes the uncertainty of absorber orientation in the cryostat.) When the absorber was cooled further to 3.8 K, R diminished by about 10% from the 4.2 K maximum, and then dropped sharply to zero (within the statistical error) in the next 0.5 K, indicating a return of Fe spins to the a axis.

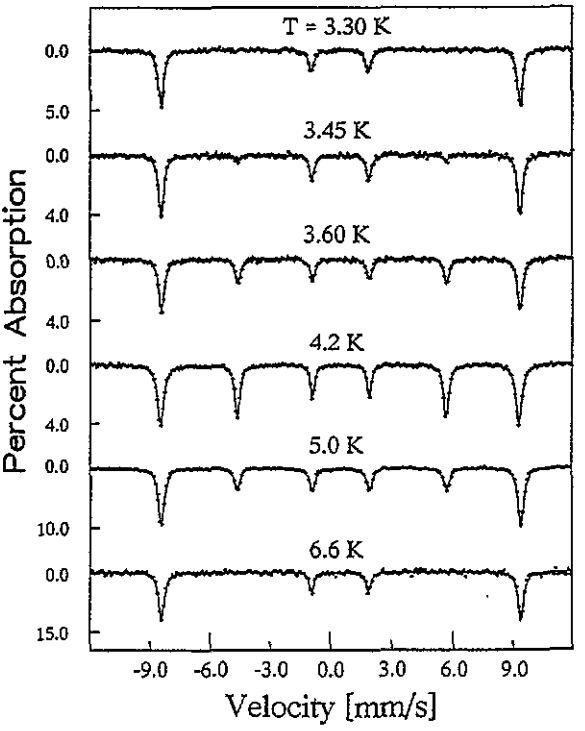

Figure 1. Mössbauer spectra from a (*bc*)-plane absorber of $TbFeO_3$ measured at various temperatures.

The temperature dependence of the quadrupole shift 2ϵ is illustrated in figure 3(a). If one neglects possible anisotropic changes of lattice parameters, the EFG components may be assumed to be constant, leaving any variation of ϵ entirely due to its angular term. Therefore,

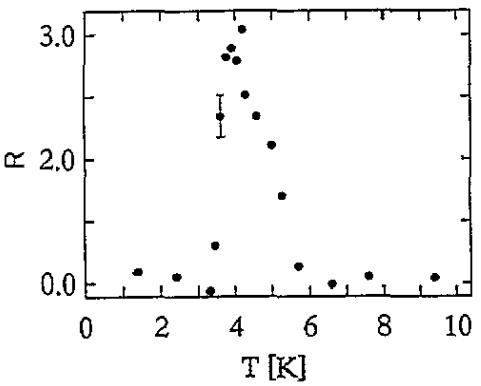

Figure 2. The temperature variation of the second and fifth Mössbauer absorption-line relative intensities from a (*bc*)-plane $TbFeO_3$ absorber.

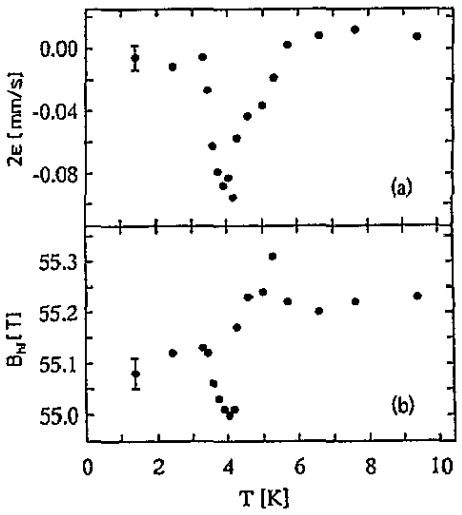

Figure 3. The temperature dependence of the hyperfine interaction parameters of the $TbFeO_3$ Mössbauer spectra obtained from a (*bc*)-plane absorber: (a) quadrupole shift 2ϵ; (b) hyperfine field B_{hf}.

the variation of the quadrupole shift on cooling the sample also shows two distinct spin rotations, one away from and the other back to the *a* axis. Basically the same pattern can be noticed as with the RLIS: the 3.3–3.8 K interval is characterized by a very sharp change, in contrast to the 4.2–6 K one.

The magnetic hyperfine field B_{hf} is plotted versus temperature in figure 3(b). Its variation is mainly due to the dipolar term that has the same angular dependence as the quadrupole shift, but an anisotropy of the *g*-factor might contribute as well. The lower-temperature sharp spin rotation can be seen very well while the other one is unclear. One reason for this might be that the hyperfine field is less sensitive to spin rotations than ϵ, because the angular-dependent terms of the former add to the much larger contact term. Another source of the partial discrepancy with the other Mössbauer parameters might be attributed to the fitting of spectra with a single-sextet model. There was a slight systematic broadening of the spectrum lines, smaller from 3.3 to 4.2 K and larger in the 4.2–5.3 K interval (figure 4) which might be an indication that more than one Zeeman sextet was present in the Mössbauer spectra measured at those temperatures. In fact, NMR experiments have shown that Fe sublattices 1 and 3 [1] in rare-earth orthoferrites become magnetically inequivalent to 2 and 4 during a continuous spin rotation (see for instance [10]). This has been seen as two hyperfine fields within the reorientation interval. The difference between them depends on the rare-earth ion and reaches a maximum of 0.37 T in $ErFeO_3$. We have no NMR data for $TbFeO_3$ and the fitting procedure was unstable with a two-sextet model so the above is only a likely explanation of the behaviour of the effective magnetic field as measured by us in $TbFeO_3$.

We suggest the following interpretation based on our experimental results reported so far. Going from higher to lower temperatures, the Fe^{3+} spins stay aligned antiferromagnetically along the *a* rhombic axis in the $\Gamma_4(G_xF_z)$ mode down to about 6 K. On further cooling the antiferromagnetic vector $\boldsymbol{G}$ starts rotating continuously towards the *c* rhombic axis. The features of this rotation are consistent with a $\Gamma_4(G_xF_z) \rightarrow \Gamma_{24}(G_{xz}F_{zx})$ reorientation. The maximum deviation from the *a* axis we found was $55° \pm 6°$ at 4.2 K. Below that temperature the Fe^{3+} spins return to the *a* axis by what appears to be a $\Gamma_{24} \rightarrow \Gamma_4$ discontinuous rotation.

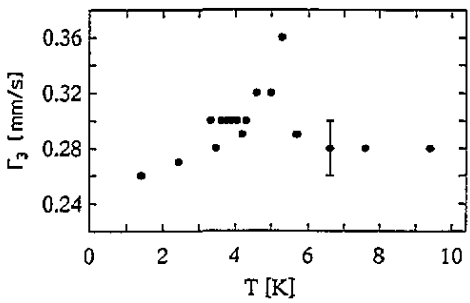

Figure 4. Full widths at half-maximum of the innermost lines of Mössbauer spectra measured with the (*bc*)-plane absorber versus temperature.

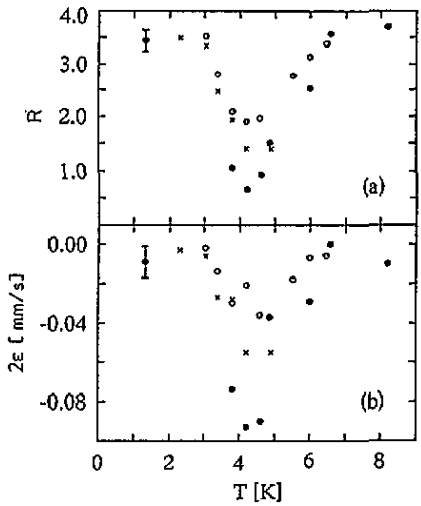

Figure 5. The temperature dependence of some parameters of Mössbauer spectra measured with the (*ab*)-plane $TbFeO_3$ absorber: (a) relative intensities of the second and fifth Mössbauer absorption lines; (b) quadrupole shift 2ϵ. Full circles (●), back of absorber glued to Be support; crosses (×), face of absorber covered with BF-2 adhesive; open circles (○), face covered with low-temperature epoxy resin.

The observed 0.5 K 'width' of the latter transition could be due to stress, defects or other inhomogeneities in the absorber. In fact it is much narrower than what has been reported in the Mössbauer literature so far. This might be evidence that the stress contribution is relatively small [9].

The (*ab*)-plane absorber showed similar behaviour with the RLI in this case starting (at 295 K) from a value close to four, as would be expected for spins perpendicular to the γ-rays. The relative 2,5-line intensities and the quadrupole shift obtained by fitting the (*ab*)-spectra are shown in figure 5. The full circles on both plots represent measurements with the absorber glued in the usual way, i.e. only its back covered with the BF-2 adhesive and attached to the Be disc. The minimum of the RLI corresponds to Fe^{3+} spins 58° away from the *a* axis, in very good agreement with the number obtained with the (*bc*) absorber, while a full 90° rotation would yield zero 2,5-line intensities.

The sample was partially damaged because of repeated thermal cycling and it became necessary to cover also its face with BF-2 to keep it as one piece. This presented us with an opportunity to see the effect of the stress induced by glues at low temperatures due to differences in thermal expansion properties. The crosses in figure 5 represent the measurements made after the additional treatment. The open circles are data points obtained with the same absorber, further covered with low-temperature epoxy resin on top of the BF-2 glue layer. As can be seen from figure 5(a) and (b), covering the absorber with BF-2 noticeably reduced the depth of the minimum, i.e. the angle between G and the *a* axis at 4.2 K, and the epoxy resin contributed further to this. If the latter had been applied directly onto the surface of the crystal or if the crystal had been embedded in it the effect might have been even stronger, since BF-2 probably acted as a buffer between them. A larger crystal such as those usually used in other techniques, e.g. neutron diffraction or magnetization

measurements, may be less affected by stress due to mounting. Indeed, the Fe^{3+} spins seem to have rotated closer to the c axis in the work of Derkachenko *et al* [13], the spontaneous magnetization along c being about 20% of that immediately above 6 K. It is possible that a completely free crystal would exhibit the full 90° spin rotation $\Gamma_4 \rightarrow \Gamma_2$. Crystal size and quality might explain some of the contradictory results reported for $TbFeO_3$ so far.

Comparing data from the (bc) and (ab) absorbers, it can be seen that the spin rotation intervals are broader in the latter case—the application of the glue broadened the interval of the sharper transition by almost a factor of two, while the higher-temperature rotation was almost unaffected. This is further indirect evidence that the former takes place locally by spin jumps while the latter is a continuous rotation, since only first-order spin-reorientation phase transitions involving phase coexistence are apparently 'broadened' by external stress [9]. No other differences were found between the two absorbers of different orientations. Our results obtained from both samples are consistent with Fe^{3+} spins along the a rhombic axis down to ~6 K.

The spin reorientations in $TbFeO_3$ are believed to have the following mechanism [11, 12]. As already mentioned, below $T_N = 681$ K the magnetic symmetry in that material is described by the *single* irreducible representation $\Gamma_4(G_xA_yF_z; f_z)$ of the D_{2h}^{16}–$Pbnm$ space group. The ground multiplet $^7F_6$ of the free non-Kramers Tb^{3+} ions is degenerate. This degeneracy is lifted by the crystalline field in rare-earth orthoferrites. The two lowest energy levels remain, however, very well separated from the next higher levels and only slightly split due to admixtures of the higher electron states [6], thus forming an apparent or quasidoublet. As has been shown by Griffith [14], the g-factor of such a doublet in even-electron ions is highly anisotropic, having a non-zero component along only one axis of an appropriately chosen co-ordinate system. In the case of Tb^{3+} this axis lies in the (ab) plane at ±36° to the a axis. A magnetic field (applied or internal) anywhere off the c axis will cause a Zeeman splitting of the rare-earth ion ground quasidoublet and hence lower the energy of the system while a field parallel to c will not have this effect. This energy reduction may occur if the Fe^{3+} spins rotate towards this axis in the (ac) plane and the ferromagnetic vector F approaches (ab). On the other hand, this is energetically unfavourable for the Fe sub-system because of its inherent anisotropy. As a result of this competition the equilibrium orientation of the Fe spins rotates continuously from a to c with reducing temperature, starting at about 6 K. When the rotation is completed, the symmetries of *both* Tb and Fe sub-systems are described again by a *single* irreducible representation $\Gamma_2(G_zC_yF_x; f_xc_y)$. At about 4.2 K, Tb^{3+} spins order antiferromagnetically in the $\Gamma_8(a_xg_y)$ mode. The Fe subsystem is still in the weakly ferromagnetic mode $\Gamma_2(G_zC_yF_x)$ [12], but since it is no longer coupled with the antiferromagnetic rare-earth sub-system it returns to its intrinsic equilibrium configuration, $\Gamma_4(G_xA_yF_z)$. No intermediate orientations of Fe^{3+} spins are possible now, and therefore the reverse rotation should really be discontinuous, possibly accompanied by co-existence of the two phases, i.e. a first-order phase transition. Our experimental data are consistent with this theoretical account of the spin rotations in $TbFeO_3$.

4. Conclusions

We have observed temperature-driven Fe^{3+} spin rotations in $TbFeO_3$ by Mössbauer spectroscopy. Our data indicate that the higher-temperature reorientation transition takes place between 4.2 and 6 K by a continuous spin rotation in the (ac) plane by an angle (from the a axis) dependent on external stress. The lower-temperature transition at about 4 K is sudden and probably inherently discontinuous.

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