Mossbauer study of field-driven spin reorientations in $YbFeO_3$ at 4.2 K

1993 J. Phys.: Condens. Matter 5 4207

(http://iopscience.iop.org/0953-8984/5/25/010)

J. Phys.: Condens. Matter 5 (1993) 4207–4214. Printed in the UK

Mössbauer study of field-driven spin reorientations in $YbFeO_3$ at 4.2 K

S R Brown and I Hall

Department of Physics, Oliver Lodge Laboratory, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

Received 14 January 1993, in final form 8 April 1993

Abstract. ^{57}Fe Mössbauer absorption spectra have been recorded at 4.2 K for various single-crystal samples of the rare-earth orthoferrite $YbFeO_3$ in applied magnetic fields up to 10 T. A field applied along the easy antiferromagnetic (c) axis induced, as expected, the Fe spins to 'flop' to being perpendicular to the field. Fields applied along the a and b crystal axes induced reorientations of the spins respectively towards and around the applied-field direction, the spins rotating towards the a axis in both cases. An explanation of these unusual reorientations is offered in terms of Fe–Yb spin decoupling.

1. Introduction

Ytterbium orthoferrite $YbFeO_3$ is a member of the rare-earth orthoferrite $RFeO_3$ family of canted antiferromagnets. These crystallize in a distorted perovskite structure with the orthorhombic space group $Pbmn$ D_{2h}^{16} [1].

The orthoferrites have Néel temperatures T_N in the 600–700 K range below which the Fe spins order with a small canting angle to the antiferromagnetic axis of approximately 10 mrad. At much lower temperatures, denoted here by $T_R \lesssim 100$ K, those orthoferrites with magnetic rare-earth ions exhibit temperature-driven spin reorientations (SR) in which the Fe spins reorient from being parallel (apart from the small canting) to the crystal a axis above T_R to being parallel to the c axis below T_R. $DyFeO_3$ is the only exception to this rule, its low-temperature phase being a purely antiferromagnetic state with the spins along the b axis. The magnetic phases may be succinctly described using the notation of Bertaut [2]. The phase with the spins along the a axis is the $\Gamma_4(G_xA_yF_z)$ configuration whereas the phase with the spins along the c axis is the $\Gamma_2(F_xC_yG_z)$ configuration†. The canting, believed to be due mainly to the antisymmetric Dzyaloshinsky–Moriya exchange interaction [3], is in the ac plane so that in both Γ_2 and Γ_4 phases these materials are weakly ferromagnetic in a direction perpendicular to the antiferromagnetic axis.

In the rare-earth orthoferrites the temperature-driven SR is actually a continuous transition centred around T_R, the temperatures at the end points of the reorientation being denoted by T_H and T_L for the higher and lower limits respectively. For $YbFeO_3$ $T_H = 7.83$ K and $T_L = 6.55$ K [4]. For $T > T_H$ the arrangement of the paramagnetic Yb spins, polarized by the Fe spins, is $\Gamma_4(O_xO_yF_z)$, i.e. net alignment parallel to the c axis. Below T_L the Yb spins have a $\Gamma_2(F_xC_yO_z)$ configuration and have been shown to lie symmetrically at

† Here, for example, G_x represents the basic antiferromagnetic arrangement of Fe spins along the a axis, A_y or C_y a canting towards the b axis, and F_z a canting towards the c axis with a non-zero magnetization in that direction.

0953-8984/93/254207+08$07.50

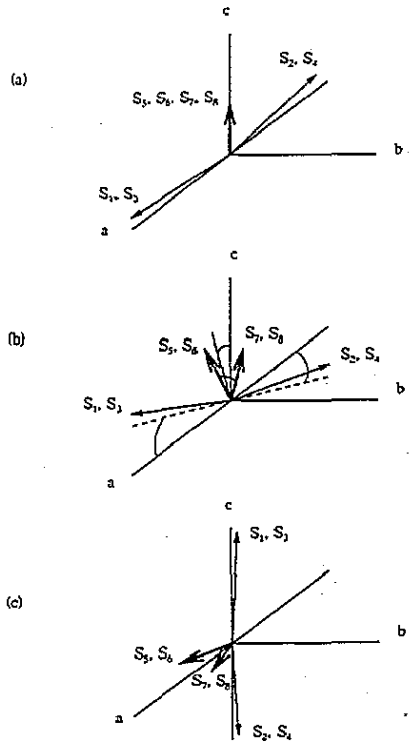

Figure 1. Configurations of the four Fe spins (S_1–S_4) and four Yb spins (S_5–S_8) per unit cell in $YbFeO_3$ (*a*) $T_H < T < T_N$, the Γ_4 phase; (*b*) $T_L < T < T_H$; (*c*) $T < T_L$, the Γ_2 phase.

27° to the *a* axis in the *ab* plane [5]. The temperature dependence of the Yb and Fe spin arrangements is shown in figure 1.

The rare-earth orthoferrites also exhibit spin-flop reorientations in applied magnetic fields. Spin-flop reorientations may occur when a field is applied parallel to the magnetic easy axis; if the anisotropy is sufficiently small the spins reorient either abruptly or gradually to being perpendicular to the applied field. Abrupt reorientations (first-order phase transitions) are characteristic of purely antiferromagnetic materials whereas canted antiferromagnets exhibit continuous reorientations (second-order phase transitions) so that the spins rotate through 90° over a finite range of applied field. Mössbauer spectroscopy is especially well suited to the study of SR as the orientation of the ionic spins is directly monitored; see, for example, earlier work on orthoferrites by Johnson *et al* [6].

Factors influencing magnetic anisotropy in the orthoferrites have been discussed by several authors. Yamaguchi [7] published a comprehensive study of the exchange interactions, whilst Moskvin *et al* [8] and Grochulski [9] concluded that both crystal-field effects and Fe–Fe dipole interactions, which are both more significant in rare-earth orthoferrites with heavier rare-earth ions, serve to stabilize the high-temperature Γ_4 phase. This is reflected in the low $\Gamma_4 \rightleftharpoons \Gamma_2$ reorientation temperature T_R in $YbFeO_3$.

This T_R ($\simeq$ 7 K) being not far above 4.2 K suggested the possibility of driving the $\Gamma_2 \rightarrow \Gamma_4$ transition with applied magnetic fields at liquid helium temperature and this is experimentally convenient. Also any effect of the polarization of the Yb spins should be pronounced at low temperature. Initial applied-field experiments at 4.2 K with a powder

$YbFeO_3$ sample indeed indicated SR effects but, at high fields, of a nature more complicated than that of a spin-flop mechanism. We were therefore led to make measurements with single-crystal absorbers with fields applied along all three crystal axes in turn. The unusual SR observed with fields applied to the *a* and *b* axes have been reported briefly earlier [10].

2. Experimental details

Experiments were conducted on three absorbers made from single-crystal samples of $YbFeO_3$ grown by the flux-growth method by R L White of Imperial College. These were prepared by cutting 1 mm thick slices from the single crystals using a diamond saw, mounting these slices on a substrate of low-temperature epoxy, and then abrading them on carborundum paper to a thickness suitable for Mössbauer absorption experiments. One absorber was a *bc*-plane sample and the other two were *ab*-plane samples. Preliminary experiments with these absorbers gave magnetic hyperfine fields of 54.8 ± 0.02 T at 4.2 K and 49.6 ± 0.02 T at room temperature in agreement with previous work [3] and also confirmed the temperature-driven SR at $T_R \simeq 7$ K.

Applied-field experiments were conducted in transverse geometry, i.e. applied field perpendicular to the γ-ray direction, this being normal to the absorber plane. For brevity we shall use a short-hand to identify a particular experimental geometry so that, for example, *bc* means use of a *bc*-plane absorber with the applied field directed along the *c* axis. For these measurements we used a 10 T superconducting-magnet cryostat (with a variable-temperature insert for experiments above 4.2 K); in addition we used a helium bath cryostat for zero-field experiments at 4.2 K or below. The spectra were recorded using $^{57}Co/Rh$ sources with constant-acceleration spectrometers operated in double-ramp (flat background) mode. Count rates in the applied-field experiments were low mainly due to the small area ($\simeq 10$ mm^2) of the single-crystal absorbers and the geometry of the magnet cryostat; consequently spectrum run times were as long as four days even with an 80 mCi source.

3. Results and discussion

In the case of a magnetically split ^{57}Fe Mössbauer spectrum there are six absorption lines; if these are labelled 1 to 6 from low energy to high energy the relative line intensity ratio for the 1,6:2,5:3,4 lines is $3 : 4\sin^2\theta/(1+\cos^2\theta) : 1$ where θ is the angle between the γ-ray direction and the magnetic field acting on the nucleus. In a zero-field experiment this is just the magnetic hyperfine field $\boldsymbol{B}_{hf}$ whose direction is determined by the Fe ion spin. In an applied-field ($\boldsymbol{B}_{app}$) experiment the nucleus senses an effective field

$$\boldsymbol{B}_{eff} = \boldsymbol{B}_{hf} + \boldsymbol{B}_{app}$$

and, in the case of an antiferromagnet with equal and opposite $\boldsymbol{B}_{hf}$ from the two sublattices, the Mössbauer spectrum shows two sextets with slightly different B_{eff}. This effective-field splitting is also dependent on the orientation of the Fe spins through the above vector addition. In the study of field-driven SR it is useful to discuss Mössbauer spectra qualitatively in terms of the two effects of line intensity and effective-field splitting. However, in quantitative spectrum fits the two effects may be incorporated into one computation; for this we have here used a program developed from the calculations of Kündig [11] in which line positions and intensities are computed as a function of the electric and magnetic hyperfine

interaction parameters and the relative orientations of B_{hf}, B_{app}, γ-ray direction and the electric-field-gradient principal axes system.

Although this spectrum computation allows for the general case of combined electric and magnetic hyperfine interactions, in the case of $YbFeO_3$ the electric quadrupole interaction is very much smaller than the magnetic dipole interaction, having negligible effect on line intensity and giving only very small shifts (much less than linewidth) in line positions. Based partly on consideration of the crystal structure and partly on preliminary fits to zero-field spectra we took the z axis of the electric-field-gradient tensor to be the crystal c axis, the asymmetry parameter η to be zero, and $eV_{zz}Q/2 = -0.08$ mm s^{-1}. An alternative hypothesis of, for example, the z axis to be the crystal a axis gave quite insignificant differences in the deduced spin angles.

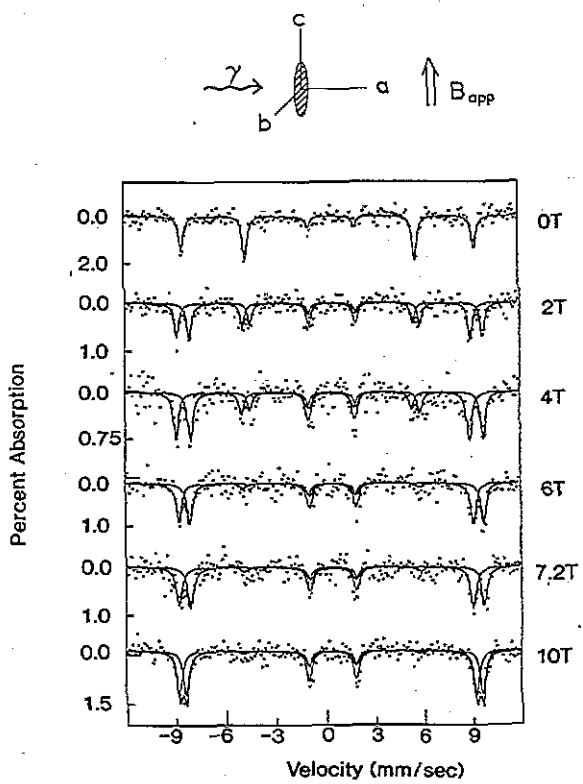

Figure 2. Mössbauer spectra taken in $b\underline{c}$ geometry at 4.2 K.

3.1. Spectra from a bc-plane absorber

Spectra taken in $b\underline{c}$ geometry (i.e. with the applied field along the magnetic easy axis) are shown in figure 2. The progression of the 2,5 line intensity and the effective-field splitting with increasing applied field is just as expected for a spin flop with the Fe spins reorienting from the Γ_2 phase to the Γ_4 phase. The spin rotation angles θ_R deduced from the fits are given in figure 3. The reorientation is seen to be gradual rather than sudden, as expected of a canted antiferromagnet. It is of experimental interest to note that, despite the limited counting statistics, the technique of the simultaneous use of line intensity and effective-field

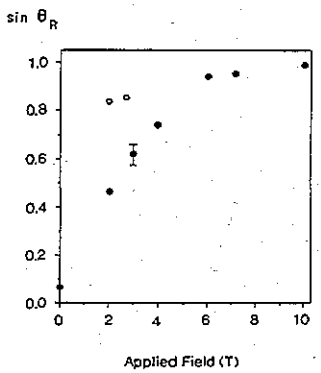

Figure 3. Spin rotation angle θ_R for $b\underline{c}$ geometry: closed circles, 4.2 K; open circles, 6.45 K.

splitting in the fitting model gives quite accurate values of θ_R, the statistical error being less than 5° at $\theta_R \simeq 45°$. The fits indicate the spins to be at approximately 7° to the *a* axis at 10 T with some of this angle possibly being due to a small experimental misalignment of the sample with respect to the field. Values for the spin rotation angle determined from spectra recorded at 6.45 K are also shown in figure 3. Smaller applied fields are required to reorient the spins at this temperature because the magnetic anisotropy decreases as T_R is approached.

3.2. Spectra from ab-plane absorbers

Experiments were conducted at 4.2 K with *ab*-plane absorbers in both $\underline{a}b$ and $a\underline{b}$ geometries, i.e. in both cases the applied field was perpendicular to the easy axis. At zero applied field the Fe spins and γ-ray direction were therefore collinear along the *c* axis, the spectra accordingly showing very little 2,5 line intensity. However, at high fields in both cases a significant 2,5 line intensity developed, indicating clearly movement of the spins away from the *c* axis. Figures 4 and 5 show spectra with the best counting statistics for the $\underline{a}b$ and $a\underline{b}$ cases respectively although similar results for both geometries were seen in both the samples used.

The $\underline{a}b$-geometry spectra showed little change up to 5 T but then the increasing 2,5 line intensity was accompanied by significant effective-field splitting, indicating that the SR was *towards* the axis of the applied field. The fit to the 10 T spectrum shows the reorientation of the Fe spins to be 43° ± 5° from the *c* axis towards the *a* axis. It is not possible to be certain that the spins stayed exactly in the *ac* plane as they reoriented away from the *c* axis although the fits indicate that they were always close to it.

In $a\underline{b}$ geometry there was already some increase in 2,5 line intensity by 5 T but throughout there was very little effective-field splitting, showing the spins to have rotated *around* the applied field but again towards the *a* axis. At 10 T the rotation angle was 73° ± 5° and greater than in the $\underline{a}b$ case, possibly because in the $a\underline{b}$ case the SR mechanism would have to overcome the normal tendency of antiferromagnetically coupled spins to lie perpendicular to an applied field. The unresolved field splitting at 10 T allows the spins being out of the *ac* plane by no more than approximately 5° and this could be a small misalignment effect.

These two SR seen with the *ab*-plane samples have, to our knowledge, not been reported before. They are different from the screw reorientations in $DyFeO_3$ [6] which involve transitions to or from the purely antiferromagnetic Γ_1 phase and also from the reorientation

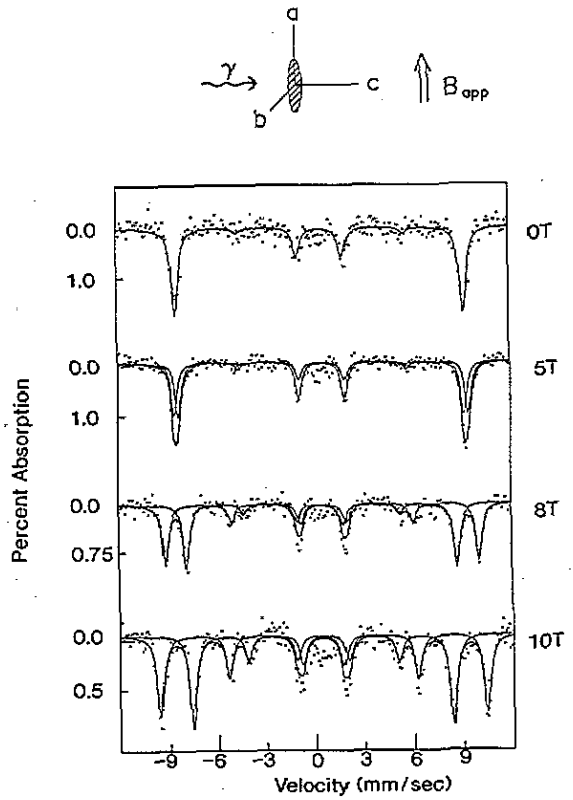

Figure 4. Mössbauer spectra taken in *ab* geometry at 4.2 K.

in $HoFeO_3$ where the Fe spins align parallel and antiparallel to a 1.5 T field applied along the *b* axis [6]. The notable feature of the reorientations in $YbFeO_3$ is that, regardless of the direction of the applied field, the Fe spins always tend to rotate towards the *a* axis. The explanation may be that the field weakens the Fe–R coupling and thus the Fe spins revert to their high-temperature configuration. It was shown by Yamaguchi [7] that the $\Gamma_4 \rightleftharpoons \Gamma_2$ SR is assisted by polarization of the R spins through a complex combination of symmetric and antisymmetric exchange. Then if, as in our case, experiments are conducted close to T_R the Fe spin configuration may be quite sensitive to weakening of the Fe–R coupling. We note that in the low-temperature phase the compatible Γ_2 configuration of the R spins, polarized by the Fe spins, is as shown in figure 1(*c*). The R spins are not collinear so that an external field, in any direction if strong enough, may break the Fe–R coupling.

Finally we comment briefly on the possibility mentioned by Dan'shin *et al* [12] of an admixture of Γ_8 into the Γ_2 configuration of the Yb spins due to increasing R–R interaction at low temperature. Such mixing might perturb the Fe spins from their Γ_2 configuration. In the case of another orthoferrite, $TbFeO_3$, Bertaut *et al* [13] have shown that the R spins actually order in a Γ_8 configuration below 3.1 K; they also suggested that the Fe spins 'probably' revert to a Γ_4 configuration on decoupling from the R spins. Although we are not aware of any published report of rare-earth ordering in $YbFeO_3$ we nevertheless took zero-field Mössbauer spectra with an *ab*-plane absorber at 2.5 K and 1.3 K. The lack of any development of 2,5 line intensity showed clearly that the Fe spin configuration is still Γ_2 down to 1.3 K in zero applied field. It therefore seems unlikely that Yb–Yb coupling

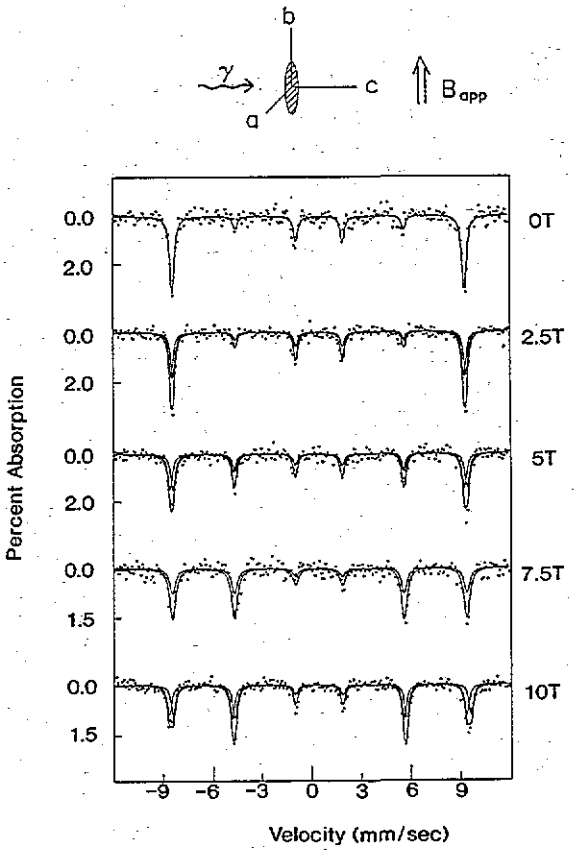

Figure 5. Mössbauer spectra taken in *ab* geometry at 4.2 K.

has a major role in the field-driven SR at 4.2 K reported here.

4. Conclusion

We have studied field-driven spin reorientation in $YbFeO_3$ at 4.2 K, just below its $\Gamma_4 \rightarrow \Gamma_2$ spin reorientation temperature, using Mössbauer spectroscopy with single-crystal absorbers and applied fields along all three crystal axes. Applied fields along the easy (c) axis induced, as expected, a $\Gamma_2 \rightarrow \Gamma_4$ spin reorientation. Unusual reorientations were observed at high fields applied along the a and b axes, the Fe spins in both cases rotating towards the a axis. It is suggested that these are due to breaking of the Fe–Yb spin coupling whereby the Fe spins revert to their high-temperature configuration.

Acknowledgments

This work was supported by the UK Science and Engineering Research Council. SRB acknowledges the support of an SERC studentship.

References

[1] Eibschütz M 1965 *Acta Crystallogr.* **19** 337
[2] Bertaut E F 1963 *Magnetism III* ed G T Rado and H Suhl (New York: Academic) p 147
[3] Eibschütz M, Shtrikman S and Treves D 1967 *Phys. Rev.* **156** 562
[4] Moldover M R, Sjolander G and Weyhmann W 1971 *Phys. Rev. Lett.* **26** 1257
[5] Davidson G R, Dunlap B D, Eibschütz M and van Uitert L G 1975 *Phys. Rev.* B **12** 1681
[6] Johnson C E, Prelorendjos L A and Thomas M F 1980 *J. Magn. Magn. Mater.* **15–18** 557
[7] Yamaguchi T 1974 *J. Phys. Chem. Solids* **35** 479
[8] Mo•kvin A S, Sinitsyn E V and Smirnov A Yu 1978 *Sov. Phys–Solid State* **20** 2002
[9] Grochulski T 1980 *J. Magn. Magn. Mater.* **15–18** 35
[10] Brown S R and Hall I 1993 *J. Phys.: Condens. Matter* **5** L99
[11] Kündig W 1967 *Nucl. Instrum. Methods* **48** 219
[12] Dan'shin N K, Zherlitsyn S V, Zvada S S, Kramarchuk G G, Sdvizhkov M A and Fil' V D 1987 *Sov. Phys.–JETP* **66** 1227
[13] Bertaut E F, Chappert J, Mareschal J, Rebouillat J P and Sivardière J 1967 *Solid State Commun.* **5** 293