A Mössbauer study of temperature-driven spin reorientations in $Dy_{1-x}Ho_xFeO_3$

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Abstract. Single crystals of the mixed rare-earth orthoferrite $Dy_{1-x}Ho_xFeO_3$ ($x = 0.25$, 0.5, and 0.75) have been studied by Mössbauer spectroscopy in the 1.3–298 K temperature range. Several temperature-induced Fe^{3+} spin reorientation transitions have been observed. On cooling, a locally discontinuous reorientation from the a to the b orthorhombic axis took place near 40 K followed by a continuous reorientation from the b to the c axis. The onset temperature of the latter transition depends linearly on Ho concentration x. An x–T phase diagram of $Dy_{1-x}Ho_xFeO_3$ is proposed which extrapolates well to the results of previous studies of pure $HoFeO_3$ and pure $DyFeO_3$. The continuous Fe^{3+} spin reorientation in the bc plane showed the hyperfine interactions of the ^{57}Fe nuclei to split into two branches. This branching is associated with different Fe unit cell positions. The temperature variation of the difference in magnetic hyperfine fields agrees well with a previous calculation of a similar effect in NMR. We also observed a new, very sharp Fe^{3+} spin reorientation from the c to the b orthorhombic axis upon cooling a $Dy_{0.75}Ho_{0.25}FeO_3$ single-crystal absorber between 3 K and 2.3 K. We suggest that this transition is driven by ordering of the rare-earth spins and a microscopic mechanism is proposed.

1. Introduction

The distorted perovskites $RFeO_3$ (R = rare earth or Y), also called rare-earth orthoferrites, are known for the rich variety of interactions between the rare-earth and Fe ions and for the number of magnetic phase transitions that occur in them. These canted antiferromagnets crystallize according to the D_{2h}^{16}–$Pbnm$ space group with four $RFeO_3$ molecules per unit cell. Just below the Néel temperature (between 600 and 800 K depending on the rare earth), the iron-spin subsystem is ordered according to the $\Gamma_4(G_xA_yF_z)$ representation of the space group, while the rare-earth ion moments are paramagnetic and polarized in a configuration belonging to the same mode, $\Gamma_4(f_z)$. (We follow the notation of Bertaut [1] and the common practice of using G, F, A, and C as basis vectors to describe the Fe^{3+} spin system and corresponding lower-case letters to describe the rare-earth system.) Physically this means that the Fe^{3+} spins are ordered antiferromagnetically along the a orthorhombic axis with a small canting off the ab plane which produces a weak ferromagnetic moment F along the c axis. The magnetic configuration of the whole system may be denoted by $\Gamma_4(G_xA_yF_z; f_z)$ to emphasize that both the Fe^{3+} and R^{3+} systems belong to the same irreducible representation. The canting is generally very small, so that the magnitude of the antiferromagnetic vector G is usually much larger than that of the ferromagnetic moment

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F and the 'weak antiferromagnetic moments' A and C. The upshot is that we can often neglect the canting and assume that G is parallel to the Fe^{3+} spins.

The interactions between the Fe^{3+} and R^{3+} ions are anisotropic and temperature dependent. In some orthoferrites this is manifest macroscopically upon cooling as a gradual change of direction of the weak ferromagnetism from the c to the a orthorhombic axis. Microscopically, the Fe^{3+} spins (and G) rotate continuously from a to c within the ac plane over a temperature interval of several K. The beginning and end of this reorientation are each marked by a second-order phase transition [2]. The final magnetic state is described as $\Gamma_2(F_x C_y G_z; f_x c_y)$. The intermediate magnetic configuration, where the Fe^{3+} spins are part-way through the continuous rotation, has a lower symmetry than the initial or final state and belongs to a subgroup of D_{2h}^{16}–$Pbnm$. It is described as Γ_{24} by Yamaguchi and Tsushima [3] and is sometimes referred to as an 'angular' phase. Mössbauer spectroscopy usually gives information mainly about the vector G. Therefore we shall also use a shorter notation such as $\Gamma_i(G_j)$ or Γ_i ($i = 1, 2, \ldots, 8$, $j = x, y, z$) instead of the full notation, omitting the components of the other basis vectors where possible.

Of those orthoferrites where a spin reorientation takes place, $DyFeO_3$ was thought until recently to be the only exception to the Γ_4–Γ_{42}–Γ_2 pattern. At about 35 K [4] it undergoes a first-order phase transition similar to the Morin transition in haematite, α-Fe_2O_3. The weak spontaneous ferromagnetic moment along the c axis vanishes and the material goes into a purely antiferromagnetic state [5]. This involves a discontinuous reorientation of the Fe^{3+} spins from the a to the b orthorhombic axis, i.e. to the $\Gamma_1(G_y)$ mode. On the other hand, $HoFeO_3$ [6] and $TbFeO_3$ [7] were considered to be classical examples of the Γ_4–Γ_{42}–Γ_2 continuous Fe^{3+} spin rotation in the ac plane. However, there are some similarities between the former and the latter two orthoferrites. In particular, the ground states of their rare-earth ions have highly anisotropic g-factors resulting in 'Ising' axes lying in the ab plane at $\alpha = \pm 36°(Tb^{3+})$, $\pm 63°(Ho^{3+})$, or $\pm 60°(Dy^{3+})$ from the a orthorhombic axis. In $TbFeO_3$ the Fe^{3+} spin rotations are confined to the ac plane. Ho^{3+} is a non-Kramers ion like Tb^{3+} but its ground-state quasidoublet g-factor resembles that of Dy^{3+}. So a reorientation of the Fe^{3+} spins from the a to the c axis in $HoFeO_3$ takes place via a complex path involving continuous rotations in the ac and bc planes with an intermediate discontinuous reorientation from one plane to the other [8–10]. Other attempts to acquire a better understanding of the Fe^{3+}–R^{3+} interactions in orthoferrites with Ising rare-earth ions have been undertaken by Belov *et al* [11, 12] and Chernenkov *et al* [13]. They employed magnetization and neutron diffraction measurements to study the solid solution $Dy_{1-x}Ho_xFeO_3$ for several values of x, and found that this system exhibits a rich mixture of the properties of pure $DyFeO_3$ and $HoFeO_3$. Now single-crystal Mössbauer spectroscopy is well suited to the study of spin reorientations because the relative line intensities in the magnetically split spectrum are directly related to the Fe^{3+} spin directions. We have therefore used this technique to study systematically the various temperature-driven spin reorientation phase transitions in $Dy_{1-x}Ho_xFeO_3$ over a range of compositions. In particular we aimed to establish the continuous or discontinuous nature of these transitions by a microscopic method and also to ascertain the dependence of transition temperatures on the relative Dy/Ho concentration.

2. Experimental procedure

Single crystals of $Dy_{1-x}Ho_xFeO_3$, $x = 0.25$, 0.5, and 0.75, were grown at the Clarendon Laboratory, Oxford, from high-purity Dy, Ho, and Fe compounds by the flux method. Microprobe analysis gave respectively $x = 0.272(2)$, 0.520(2), and 0.755(2) where the

bracketed number in each case is the root mean square deviation evaluated over several points of the crystal sample. We will refer to the three compositions by their nominal values. Slices in appropriate planes were abraded down to about 35 μm and then had both faces polished by 0.3 μm diamond paste to reduce the surface damage created by cutting and grinding. The plates thus prepared were glued to Be discs by BF-2 adhesive. All absorbers were finally checked by Laue diffraction and were found to deviate from the desired orientation by less than 1°. The usable areas varied between 0.2 and 0.5 cm^2.
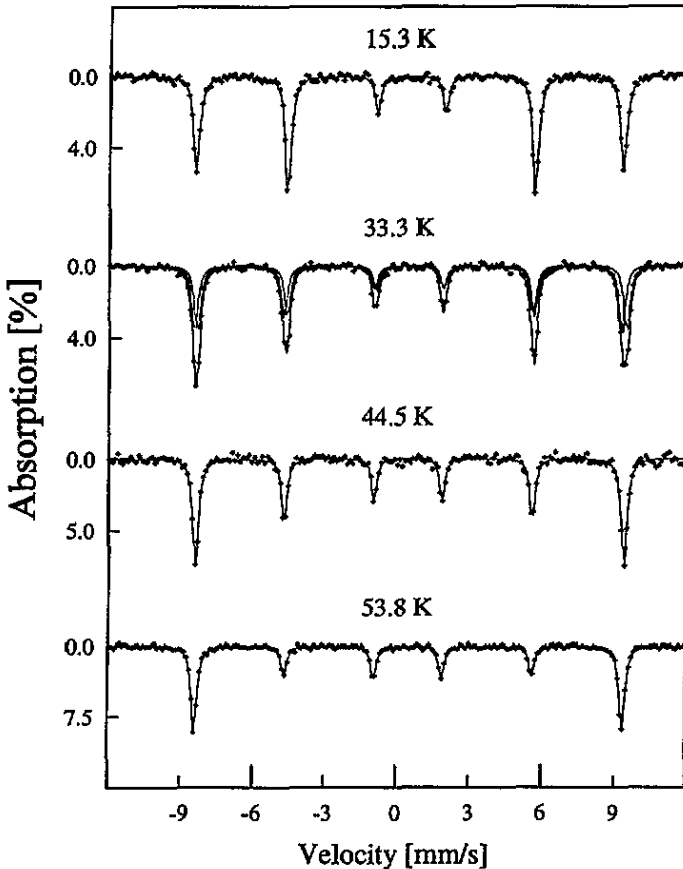

Figure 1. Mössbauer spectra from a (110)-plane absorber of $Dy_{0.25}Ho_{0.75}FeO_3$ measured at various temperatures.

The relative line intensities in Mössbauer spectra play an important part in the study of spin reorientations. We recall that, in a magnetically split (six-line) Mössbauer spectrum, the 1,6:2,5:3,4 line intensity ratios are 3:R:1 where

$$R = 4\sin^2\theta(1+\cos^2\theta)^{-1}$$

and θ is the angle between the γ-ray direction and the magnetic field acting on the nucleus. The latter is in turn determined by the ion spin. Thus in the case of a bc-plane absorber, for example, an $a \rightarrow b$ spin reorientation would result in R changing ideally from zero to four.
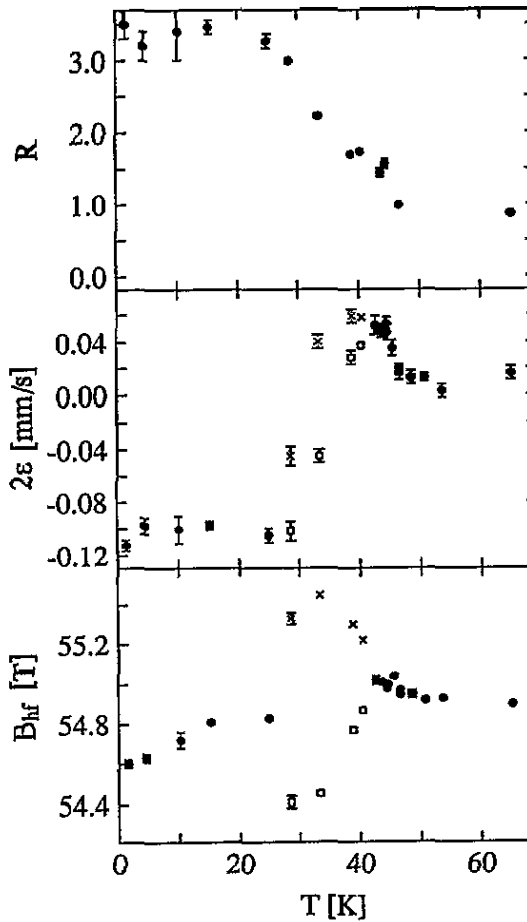
Figure 2. The temperature variation of the Mössbauer spectral parameters from a (110)-plane single-crystal absorber of $Dy_{0.25}Ho_{0.75}FeO_3$: the relative line intensity R, the quadrupole shift 2ε, and the hyperfine field B_{hf}. ●, collinear phase; × and □, angular phases (see text).

However, if this change were gradual it would not necessarily signify a second-order phase transition. An inherently first-order (abrupt) transition might appear continuous because inhomogeneity in the crystal may distribute the locally abrupt transition over a range of temperature. For this reason much of the present work has been done with (110)-plane absorbers with which it is possible to distinguish between true and apparent continuous transitions. With such an absorber a truly continuous transition would have the Fe^{3+} spins rotating from a to b giving part-way a clear minimum or maximum in R depending on the sense of the rotation [14, 15]. The extremum would be more or less pronounced depending on the domain structure of the absorber in the angular phase [16, 17]. By contrast, a first-order transition would have the spins jump from a to b—not necessarily all at the same temperature because of inhomogeneity—giving a small monotonic change in R. This change may be measurably non-zero because of the sensitivity of R at $\theta \approx 45°$ and because the initial and final θ are not exactly the same due either to the small difference in the a and b lattice constants [18] or to slight experimental misalignment.

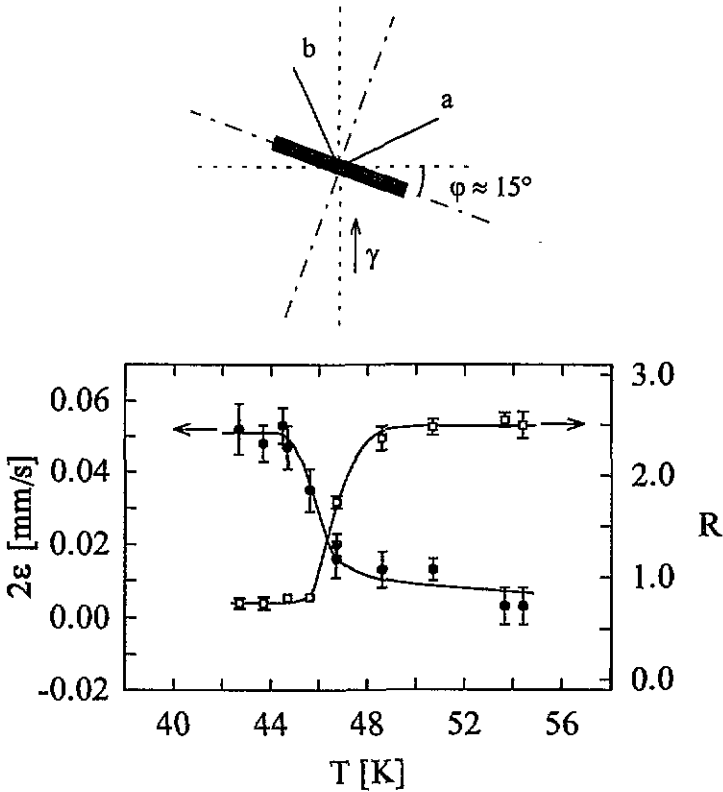Although a polarized source may alternatively be used to determine the nature of spin

Figure 3. The higher-temperature spin reorientation in Dy$_{0.25}$Ho$_{0.75}$FeO$_3$ measured with a special orientation of the (110)-plane absorber. ●, quadrupole shift parameter 2ε; □, relative line intensity R. The lines are guides to the eye only.

reorientations, the method described here has some advantage in simplicity and also in yield, bearing in mind the strong electronic absorption of these materials.

Most of the measurements were carried out with an Oxford Instruments continuous He gas flow cryostat from 4.3 K to room temperature. The temperature was maintained by an ITC-4 temperature controller and was measured independently on the sample holder by a carbon glass resistor and a resistance bridge, the deviation being found to be normally less than 0.05 K at temperatures below 60 K. Measurements were also taken below 4.2 K in a helium bath cryostat with pumping facilities. The temperature was determined from the pressure above the liquid and was stable within less than 0.002 K at 3–4 K and 0.01 K at 1.3 K.

The Mössbauer spectrometers were set up in constant-acceleration mode, and spectra were accumulated in transmission geometry, using ^{57}Co(Rh) sources. All least-squares fits to the experimental spectra were done using models of one or two Zeeman sextets with Lorentzian lines and in the approximation of a strong effective magnetic field perturbed by a weak quadrupole interaction.

3. Experimental results

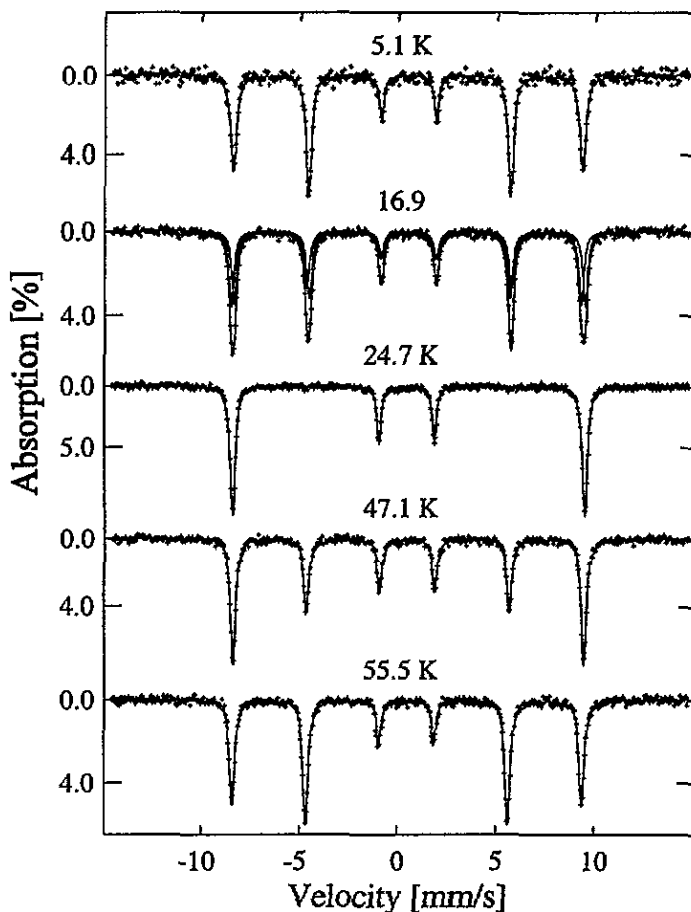We report the results for the three concentrations in turn.

Figure 4. Mössbauer spectra from an *ac*-plane absorber of $Dy_{0.5}Ho_{0.5}FeO_3$ measured at various temperatures.

3.1. $Dy_{0.25}Ho_{0.75}FeO_3$

A (110)-plane absorber was used between 1.38 K and room temperature. Figure 1 shows some spectra taken with this absorber and the Mössbauer parameters obtained by least-squares fitting are plotted against temperature in figure 2. As the sample is cooled the line intensity ratio R shows spin reorientation to occur through the 48–25 K region. Left–right asymmetry in the spectra suggested the presence of two sextets between 40 and 28 K. The temperature dependence of the quadrupole shift parameter 2ε revealed one small but significant sharp change at approximately 46 K which correlated with a slight change in R. For confirmation we ran a second set of measurements closely spaced in temperature around 46 K, with the absorber deliberately rotated by approximately 15° about the c axis as shown in figure 3. This figure shows a sharp change in R matched by one in 2ε. The quadrupole shift remained positive, varying from +0.01 to +0.05 mm s^{-1}, values similar to those reported previously for $DyFeO_3$ with Fe^{3+} spins along its a and b axes respectively [15, 19]. There was no sign of a minimum or a maximum in R with either absorber orientation. We think the small change at $T \approx 46$ K in R in figure 2 is due to a small difference in the a and b lattice parameters as described earlier together possibly with some misalignment of
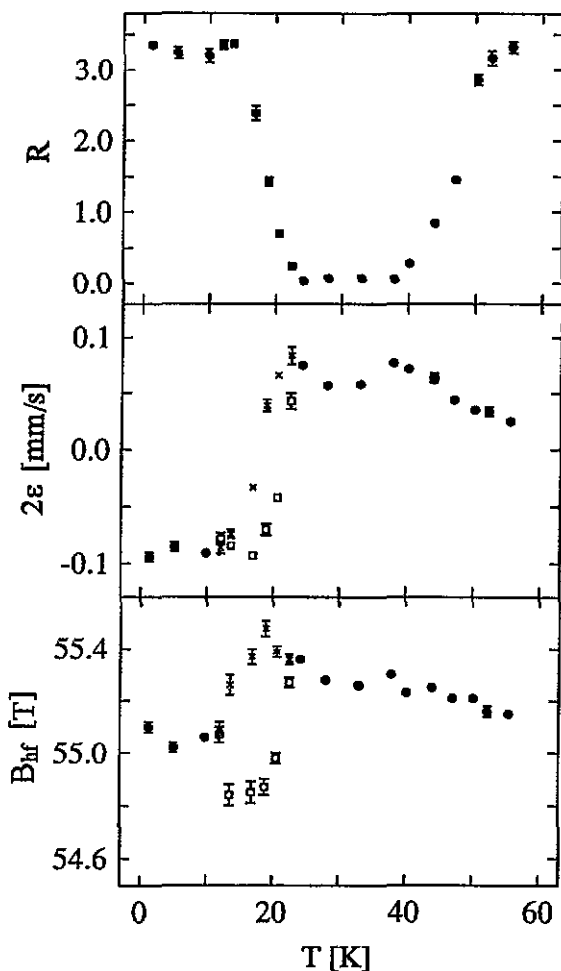
Figure 5. The temperature variation of the Mössbauer spectral parameters from an *ac*-plane single-crystal absorber of $Dy_{0.5}Ho_{0.5}FeO_3$. ●, collinear phases; × and □, angular phases.

the absorber in the cryostat. We conclude that this spin reorientation is discontinuous from the *a* to the *b* axes, i.e. a $\Gamma_4(G_x)$–$\Gamma_1(G_y)$ phase transition. It was not possible to obtain reliable fits of a two-sextet model to the spectra in the region of this transition, presumably because the hyperfine-interaction parameters in the two spin alignments differ very little. Therefore the values of all spectral parameters presented in figures 2 and 3 in the region of the higher-temperature Fe^{3+} spin reorientation have been derived from single-sextet fits.

Upon further cooling, another spin reorientation started almost immediately and spread from approximately $T_H \approx 42$ K to $T_L \approx 25$ K. With decreasing temperature R increased continuously to almost 3.5 which, bearing in mind a possible thickness effect, might signify spins in the absorber plane, i.e. (110). As mentioned above, two sextets were required to fit satisfactorily the spectra in this temperature interval. The relative weights of the two sextets varied randomly with temperature about a ratio of 1:1, so this ratio was fixed in the final fitting. The quadrupole shift 2ε and the hyperfine magnetic field B_{hf} also varied slowly compared with the higher-temperature spin reorientation (figure 2). They exhibited
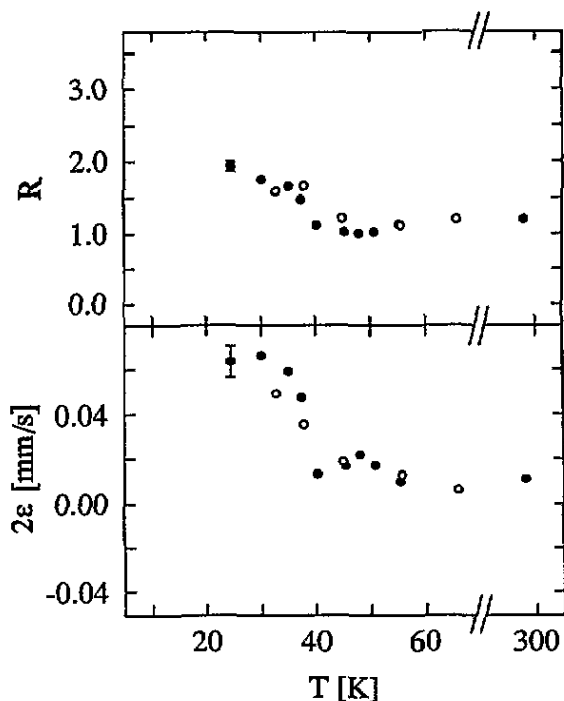
Figure 6. The upper-temperature spin reorientation in $Dy_{0.5}Ho_{0.5}FeO_3$ measured with a (110)-plane single-crystal absorber. The two symbols signify two sets of measurements.

splitting patterns in their temperature dependence which resembled the splitting of the NMR frequency during spin reorientation transitions in $RFeO_3$ (see for instance [20]). We shall discuss this matter later. The quadrupole shift 2ε reached -0.1 mm s^{-1} below 25 K, equal to that found in $HoFeO_3$ in the $\Gamma_2(G_z)$ phase [10]. This parameter is known to become negative and tend towards the same value when spins are near the c axis in $TbFeO_3$ [21] and doped $DyFeO_3$ [19]. We conclude that the Fe^{3+} spins rotated continuously in our sample between 42 and 25 K from the $\Gamma_1(G_y)$ arrangement of spins along the b orthorhombic axis to the $\Gamma_2(G_z)$ phase with spins along c. The latter configuration remains stable down to 1.3 K.

3.2. $Dy_{0.5}Ho_{0.5}FeO_3$

Several Mössbauer spectra from an ac-plane absorber are shown in figure 4 and fitted parameters are plotted in figure 5. The temperature dependence of R shows two spin reorientations very clearly. R is almost the same at high and low temperatures, presumably corresponding to Fe^{3+} spins in the ac plane. This supports our previous conclusion that upon cooling the Fe^{3+} spins reorient from the a orthorhombic axis firstly to b and then to c.

The data from this absorber show not only different transition temperatures from those from the $x = 0.75$ absorber but also a larger width (≈ 15 K) of the higher-temperature transition. This is seen in the plots of both R and 2ε. The latter remains positive through the higher-temperature transition, reflecting the Fe^{3+} spin reorientation in the ab plane.

To check the nature of the higher-temperature transition, we used also a (110)-plane absorber of $Dy_{0.5}Ho_{0.5}FeO_3$, cut from another single crystal from the same batch. The
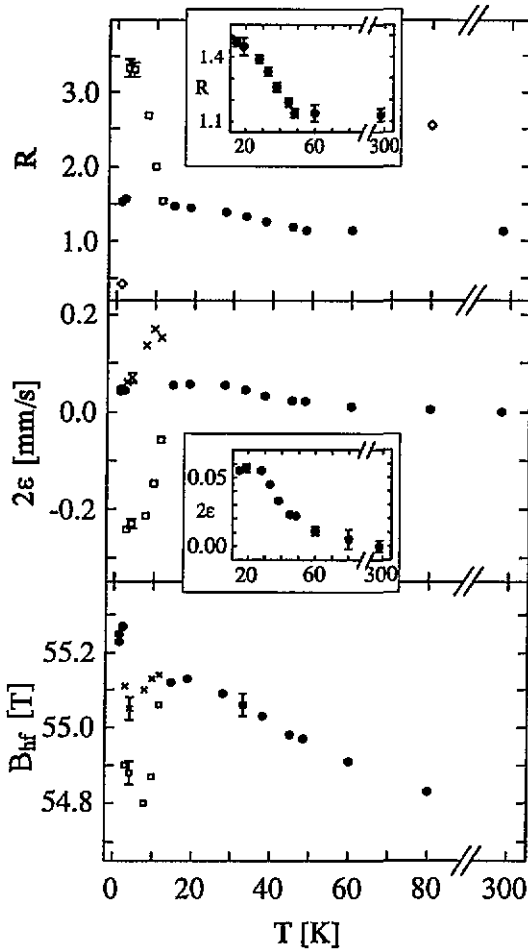
Figure 7. The temperature variation of the Mössbauer spectral parameters from a (110)-plane single-crystal absorber of $Dy_{0.75}Ho_{0.25}FeO_3$. ●, collinear phases; × and □, angular phases; ◊, R from the absorber turned by $\approx 20°$ around the c axis (see also figure 3). The inserts show the data above 10 K with an expanded vertical scale.

results of two sets of measurements of this reorientation are shown in figure 6. Again, R does not go through a significant local minimum or maximum anywhere between 35 and 55 K. This suggests that the Fe^{3+} spins also in this composition turn from a to b by a discontinuous spin reorientation.

The lower-temperature spin reorientation took place between approximately $T_H \approx 24$ K and $T_L \approx 12$ K. It exhibited the same pattern of R, 2ε, and B_{hf} temperature variation as found for the $x = 0.75$ case.

3.3. $Dy_{0.75}Ho_{0.25}FeO_3$

Figure 7 shows the temperature dependence of the fitted spectral parameters obtained with a (110)-plane absorber. A slight increase of R was observed as the absorber was cooled between 50 and 20 K. This change was matched by the quadrupole shift varying from
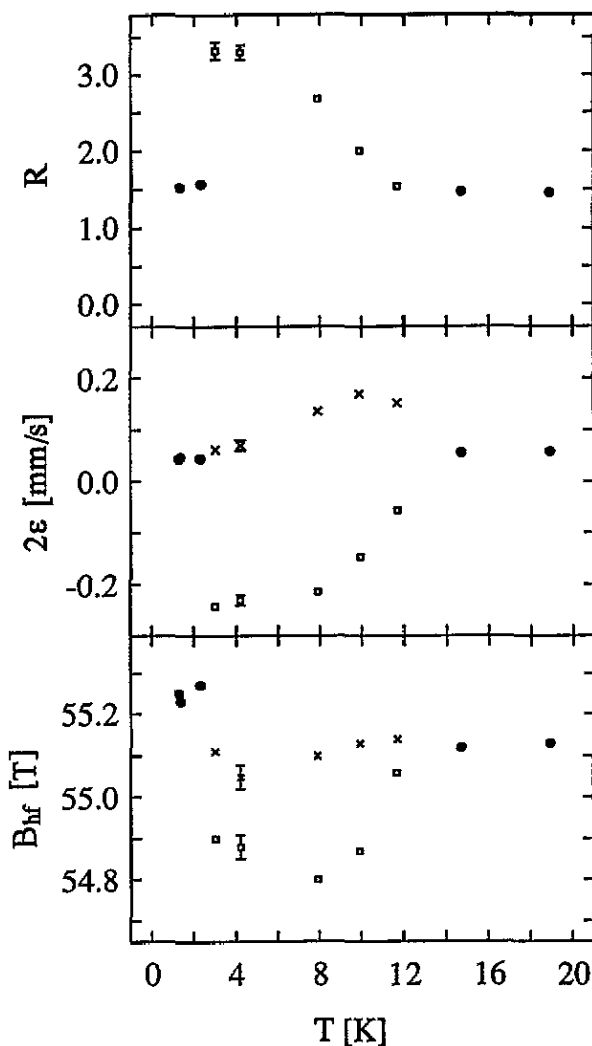
Figure 8. Low-temperature spin rotations in $Dy_{0.75}Ho_{0.25}FeO_3$ measured with a (110)-plane single-crystal absorber. ●, collinear phases; × and □, angular phases.

0.011(3) mm s^{-1} at 60 K to about 0.055(5) mm s^{-1} at 15 K. The monotonic pattern of change in R in this temperature interval again is consistent with a discontinuous spin reorientation from the a to the b orthorhombic axis.

At temperatures below $T_H \approx 12$ K the increasing value of R showed the Fe^{3+} spins to be rotating towards the absorber plane. Two sextets with different hyperfine parameters could be resolved as described previously for the other compositions. R, 2ε, and B_{hf} are plotted against T in this region in figure 8. It can be seen that two sextets were present in the spectra even at 4.2 and 3 K. Evidently the Fe^{3+} spins had not yet reached the c axis at 3 K. However, the values of R and the arithmetic mean (≈ -0.1 mm s^{-1}) of the two respective values of 2ε suggest that the $\Gamma_1(G_y)$–$\Gamma_2(G_z)$ continuous spin rotation was almost complete.

Then, at some temperature between 2.3 and 3 K, the Fe^{3+} spins suddenly reversed away
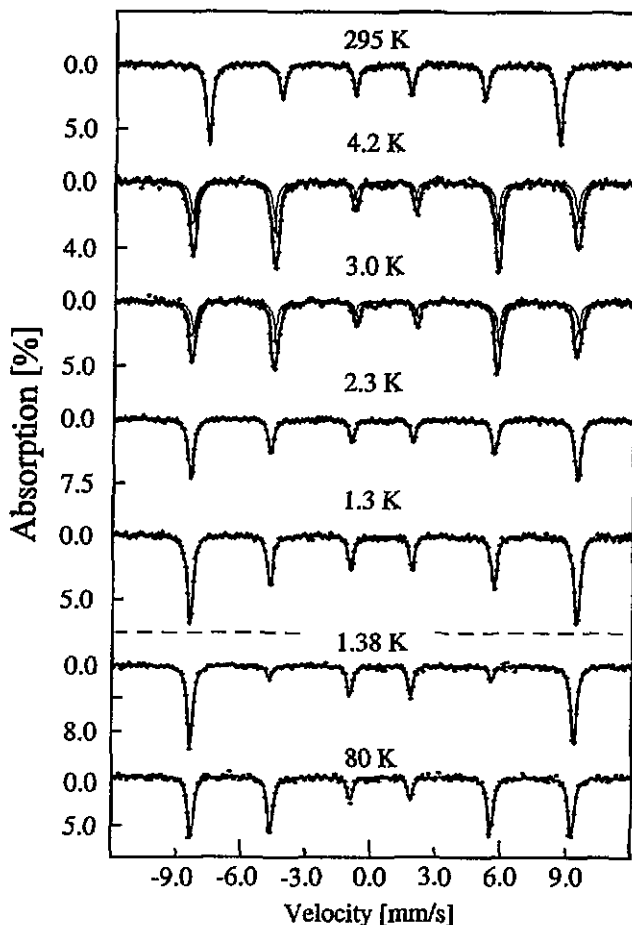
Figure 9. The lowest-temperature spin reorientation transition in $Dy_{0.75}Ho_{0.25}FeO_3$ as seen in the Mössbauer spectra from a (110)-plane single-crystal absorber. The 1.38 K and 80 K spectra were measured with the sample turned by $\approx 20°$ around its c axis. (See also figure 3.)

from the c axis: R dropped back to approximately 1.5 and the spectrum reverted to only one sextet. Some Mössbauer spectra illustrating this spin reorientation are shown in figure 9. The quadrupole shift indicated that the spins of the iron sublattice had gone back to near the b orthorhombic axis. To confirm this, we rotated the absorber around its c axis by $\approx 20°$ and measured one spectrum at 1.38 K and one at 80 K, both of which are also shown in figure 9. The corresponding values of R are shown in figure 7. This latter experiment proved that indeed the Fe^{3+} spins had gone back to the b axis in a rather sharp transition, presumably $\Gamma_{21}(G_{zy})$–$\Gamma_1(G_y)$.

4. Discussion

4.1. Theoretical background

The ground multiplet $^5I_8$ of the free non-Kramers Ho^{3+} ion is degenerate but becomes split into singlets by the crystalline field in $HoFeO_3$. The two lowest of them have energies

$E_{A,B} = E_0 \pm \Delta E_0$ ($2\Delta E_0 \approx 3.4$ cm^{-1}) and are separated by more than 80 cm^{-1} from the next higher energy level [22]. Griffith [23] has shown that the g-factor of such an apparent doublet (quasidoublet) is highly anisotropic. In the case of HoFeO$_3$ this results in 'Ising' axes in the ab plane at $\alpha = \pm 63°$ from the a orthorhombic axis. Thus a magnetic field in any direction which is not perpendicular to these axes will induce some additional Zeeman splitting of the Ho^{3+} ground-state quasidoublet The free energy of the system therefore has a minimum when $G \| c$. On the other hand, the Fe spin subsystem itself prefers energetically the $\Gamma_4(G_x A_y F_z)$ phase. As the crystal is cooled, however, the holmium ions become sufficiently polarized for their ground splitting to compensate for the Fe anisotropy. A rotation of G (Fe^{3+} spins) from the a towards the c axis then occurs in the ac plane, starting from $T_H \approx 58$ K in pure HoFeO$_3$ [8].

In other orthoferrites this continuous reorientation ends with G parallel to c at a temperature T_L typically a few K lower than T_H. HoFeO$_3$ turns out to be different [8–10]. At a temperature $T_M \approx 51$ K [8] the Fe^{3+} spins, before having reached the c axis, reorient discontinuously from the ac to the bc plane, and then reach the c axis at $T_L \approx 39$ K [8] by another continuous rotation. The mechanism behind the first-order phase transition Γ_{24}–Γ_{21} is a slight lowering of the Ho^{3+} ground quasidoublet as a whole due to weaker Van Vleck interactions with the excited levels. This mechanism is also responsible for the Morin transition $\Gamma_4(G_x F_z)$–$\Gamma_1(G_y)$ at about $T_M \approx 35$ K [4] in DyFeO$_3$. The lowest energy levels of Dy^{3+} in that orthoferrite form a $|\pm\frac{15}{2}\rangle$ Kramers doublet [5,24] which is separated from the first excited doublet by $D_1 \approx 70$ K. As already noted, the ground-state g-factor is similar to that of the lowest quasidoublet in Ho^{3+}, the angle from the a axis being $\alpha \approx 60°$ instead of 63°. It is this orientation of the Ising axes close to b which makes the Γ_4–Γ_1 transition possible. Zvezdin and Matveev [25] have shown that E_0 is modified by a quantity which depends on G_ζ, the component of G along the Ising axis:

$$\Delta E_{VV} \propto -\tanh\left(\frac{D_1}{2T}\right) G_\zeta^2. \qquad (1)$$

It is clear from (1) that the energy of the system is lowered by this temperature-dependent Van Vleck correction when G switches from the a to the b axis in DyFeO$_3$. On the other hand, the Zeeman splitting in DyFeO$_3$ is insufficient to cause an $a \rightarrow c$ iron spin rotation. Both mechanisms work in HoFeO$_3$ and their interplay brings about the Γ_4–Γ_{24}–Γ_{21}–Γ_2 sequence of spin reorientations [9].

In the case of the Dy$_{1-x}$Ho$_x$FeO$_3$ system, the Van Vleck lowerings of the ground-state doublet of Dy^{3+} and quasidoublet of Ho^{3+} combine to cause a reorientation of G from the a to the b orthorhombic axis. As the transitions in the pure orthoferrites are very close (35 K and 48–50 K respectively) the Γ_4–Γ_1 reorientation temperature in the mixed system should not depend strongly on Ho concentration x. On the other hand, the relatively large anisotropy of the Ho^{3+} ground-state quasidoublet splitting seems to be the driving force behind the lower-temperature continuous Fe^{3+} spin rotation from b to c. Indeed, there is no reorientation of G outside the ab plane in pure DyFeO$_3$. Therefore the temperature T_H at which this reorientation starts ought to depend on Ho concentration. Chernenkov et al [13] have concluded that it should be directly proportional to x.

4.2. The Γ_4–Γ_1 and Γ_1–Γ_2 transitions

On cooling, the Fe^{3+} spins reorient from the a to the b orthorhombic axis. This locally discontinuous Γ_4–Γ_1 transition was observed to spread over some temperature interval (ΔT). It is followed by a continuous Γ_1–Γ_2 spin rotation in the bc plane.

There was no evidence in our data of a continuous rotation of G from a to b out of the ab plane, as reported by Chernenkov *et al* in [13] for $x = 0.75$. On the contrary, in our work this transition was the sharpest of all: $\Delta T(x = 0.75) \approx 2$ K. For the other two compositions the transition temperature interval was wider: $\Delta T(x = 0.5) \approx 13$ K and 8 K for the ac- and (110)-plane absorbers respectively; $\Delta T(x = 0.25) \approx 22$ K.

Chernenkov *et al* [13], using calculations of Sinitsyn and Bostrem [26], have argued that randomness in the Ho^{3+} and Dy^{3+} occupation of lattice sites could cause local fluctuations of the anisotropy constants and this could broaden the observed transition interval. However, the considerable variation in ΔT suggests that this is not the principal reason for the transition width. The microprobe analysis (section 2) shows that Dy/Ho inhomogeneity over the crystal dimension is too small to be the reason either. It therefore seems that defects or stress are the most likely causes. Although we have no quantitative estimates of these effects, it should be borne in mind that the Van Vleck anisotropy in the ab plane of DyFeO$_3$ and HoFeO$_3$ is small so that the transition is sensitive and rarely appears sharp.

The midpoint temperature $\bar{T}$ of the Γ_4–Γ_1 transition is plotted in figure 10. The Morin temperature in pure DyFeO$_3(x = 0)$ has been found variously in the 30–42 K range. For our purpose here we have taken a value 35 K reported in a Mössbauer experiment by Prelorendjo *et al* [4] on an absorber prepared in similar fashion to those used in the present work. For the mixed orthoferrite ($0.25 \leqslant x \leqslant 0.75$) we have taken for consistency the values of $\bar{T}$ measured with (110)-plane absorbers. The Γ_{42}–Γ_{21} reorientation temperature in pure HoFeO$_3(x = 1)$ has been taken from the AFM resonance measurement by Balbashov *et al* [8] where it is well defined. The straight line is a fit to the points from the present work only and although we do not attach great significance to the parameters of this fit, the agreement with the Γ_{42}–Γ_{21} reorientation in pure HoFeO$_3$ is notable.
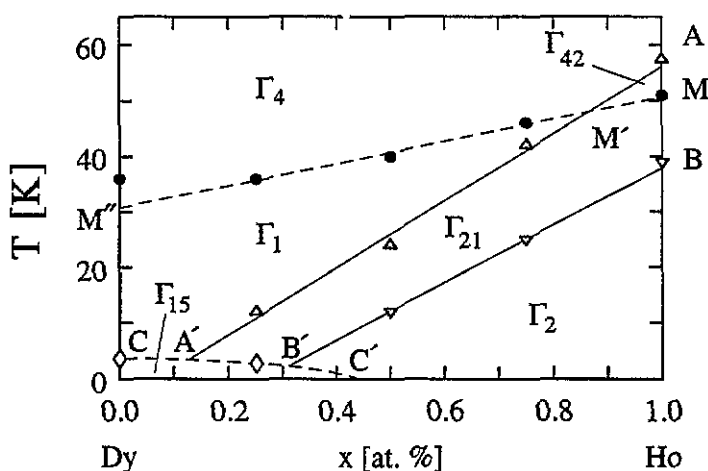

Figure 10. Dy$_{1-x}$Ho$_x$FeO$_3$: x–T phase diagram: ●, $\bar{T}$; △, T_H; ▽, T_L; ◇, $T_{N,R}$. The straight lines are fits as described in the text.

We identify the lower-temperature Fe^{3+} spin rotation as a continuous $\Gamma_1(G_y)$–$\Gamma_2(G_z)$ transition, as did Chernenkov *et al* [13]. The temperature extremes of this reorientation, $T_H(\Gamma_1 - \Gamma_{12})$ and $T_L(\Gamma_{12} - \Gamma_2)$, varied considerably with holmium concentration x, more than had been reported earlier [13]. The experimental dependence of T_H and T_L on x is also plotted in figure 10. The values for $x = 1$ are taken from [8]. Again pure HoFeO$_3$ is

included here because the spin rotation considered is out of the ab plane in all cases and is caused by the additional splitting of the ground-state quasi-doublet of Ho^{3+} as the Fe^{3+} spins approach the c axis. The agreement with the predicted relationship $T_H \propto x$ [13] is good. T_L also appears to be proportional to x. Figure 10 is in fact an x–T phase diagram of $Dy_{1-x}Ho_xFeO_3$. The broken line M–M'–M'' is a first-order phase transition line, M–M' marking the $\Gamma_{42}(G_{xz})$–$\Gamma_{21}(G_{yz})$ transition and M'–M'' the $\Gamma_4(G_x)$–$\Gamma_1(G_y)$ transition. The continuous lines are lines of second-order phase transitions: $\Gamma_4(G_x)$–$\Gamma_{42}(G_{xz})$ (A–M'); $\Gamma_{21}(G_{zy})$–$\Gamma_1(G_y)$ (M'–A'); $\Gamma_{21}(G_{zy})$–$\Gamma_2(G_z)$ (B–B').

4.3. The Fe^{3+} spin reorientation in $Dy_{0.75}Ho_{0.25}FeO_3$ below 3 K

As already noted, this was a reorientation from the c to the b axis with decreasing temperature. A $\Gamma_2(F_xG_z)$–$\Gamma_1(G_y)$ reorientation (of Cr^{3+} spins) upon cooling has been observed so far only in $NdCrO_3$ at 35 K [27]. We suggest that the mechanism in the present case originates in the ordering of the rare-earth spin system which takes place in some orthoferrites at very low temperatures. This happens in the case of both pure $HoFeO_3$ and $DyFeO_3$. In the former case the Ho^{3+} spins are known to order at approximately 6 K in the $\Gamma_2(f_xc_y)$ mode and to be aligned parallel to the two Ising axes at $\alpha = \pm63°$ from the a orthorhombic axis [18]. The Fe^{3+} spin arrangement is unchanged, being already in the Γ_2 phase. When the Dy^{3+} spins order at approximately 3.7 K in pure $DyFeO_3$, presumably according to $\Gamma_5(g_xa_y)$ as in $DyAlO_3$ [28], the Van Vleck interaction still provides a lower energy of the system if the Fe^{3+} spins are aligned along b rather than a due to the proximity of the Ising axis to b, so the iron subsystem remains in the $\Gamma_1(A_xG_yC_z)$ phase [5, 29, 3].

We propose the following mechanism for the transition in $Dy_{0.75}Ho_{0.25}FeO_3$, assuming for simplicity that the preceding $\Gamma_1 \rightarrow \Gamma_2$ transition is complete.

The Fe subsystem is ordered according to $\Gamma_2(F_xG_z)$ near 4.2 K; the rare-earth spin system is also in the Γ_2 phase. Then, somewhere near 3 K, the latter orders firstly according to the 'mixed' mode $\Gamma_{25}(f_xg_xc_ya_y)$ due to the effect of the Fe spin system still in $\Gamma_2(F_xG_z)$. The rare-earth system susceptibility is reduced because of the appearance of the g_x moment so that, in a manner similar to the one described for $TbFeO_3$ [30], there is less interaction with the Fe system and the b axis becomes once again energetically advantageous for G. The Fe spin subsystem reorders in the $\Gamma_1(G_y)$ phase again at some point between 3 K and 2.3 K. Simultaneously, the rare-earth subsystem orders in the $\Gamma_5(g_xa_y)$ mode.

By analogy with $TbFeO_3$ the $\Gamma_2(F_xG_z)$–$\Gamma_1(G_y)$ transition could be first order [30]. We include it in the phase diagram in figure 10 as a dashed line CA'B'C' which passes through $x = 0$, $T_{N,R} \approx 3.7$ K and $x = 0.25$, $T_{N,R} \approx 2.8$ K. If the mechanism proposed is correct, this should be a Morin transition and the vanishing of magnetization should easily be observed by other methods. We point out, however, that although our Mössbauer experiments are insensitive to F and f, the existence of the transition is unambiguous.

4.4. Anisotropy of the ^{57}Fe hyperfine interactions

It is not uncommon to find two sextets coexisting in a Mössbauer spectrum in a discontinuous spin reorientation. On the other hand, it is often assumed that if there is only one sextet in the Mössbauer spectrum of a magnetic material undergoing a spin reorientation, then it is a continuous rotation. However, this may not always be true. This point is well illustrated in the present work and we therefore discuss it briefly here.

Karnachev et al [20] found that the NMR signal from various orthoferrites split into two branches during the continuous Γ_4–Γ_2 transitions. This was attributed to violation of the equivalence of the four Fe sites in the unit cell in the transition region, positions 1 and 3

being different from positions 2 and 4. The effect has also been observed in Mössbauer spectroscopy [10] but it is more clearly resolved in the present data than in the earlier Mössbauer work. Of course, this site inequivalence immediately explains the equal intensity of the two branches mentioned in section 3.1. The differences $\Delta B_{hf} = B_{hf}^{(1)} - B_{hf}^{(2)}$ and $\Delta \varepsilon = 2\varepsilon^{(1)} - 2\varepsilon^{(2)}$ are plotted in figure 11. It should be borne in mind that the continuous spin rotation in Dy$_{0.75}$Ho$_{0.25}$FeO$_3$ is not finished on the lower-temperature side.
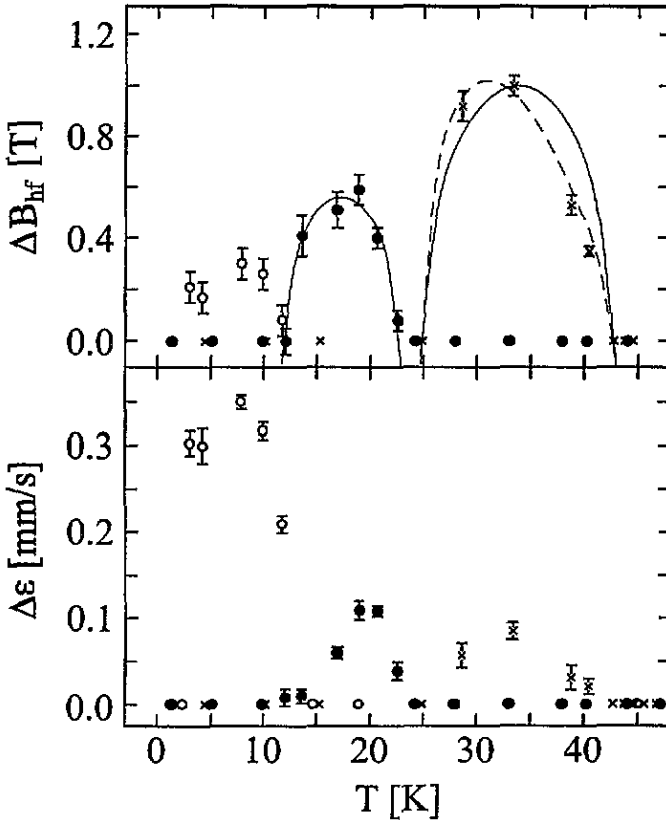

Figure 11. Top: differences between the magnetic hyperfine fields of the two components in the angular phase in Dy$_{1-x}$Ho$_x$FeO$_3$. The curves are fits based on the formula of Karnachev *et al* [20]: continuous, $\beta = 0$; broken, $\beta = 0.4$. Bottom: differences between the quadrupole shifts in Dy$_{1-x}$Ho$_x$FeO$_3$. O, $x = 0.25$; ●, $x = 0.5$; ×, $x = 0.75$.

Karnachev *et al* [20] have shown that the NMR frequency splitting in the region of a continuous $\Gamma_4(G_x)-\Gamma_2(G_z)$ spin rotation in RFeO$_3$ has the form

$$\Delta F = (\alpha + \beta \cos 2\theta) \sin 2\theta$$

where θ is the angle between the antiferromagnetic moment G and the c axis. The above function is plotted also in figure 11 for the cases of $x = 0.5$ and 0.75, in which the $\Gamma_1(G_y)-\Gamma_2(G_z)$ spin rotations are complete. Although Mössbauer spectroscopy is not as sensitive to this effect as NMR, the agreement is satisfactory. In the case of Dy$_{0.25}$Ho$_{0.75}$FeO$_3$, setting the rare-earth-related parameter β to 0.4 agrees with the experimental data better than $\beta = 0$,

which indicates that Ho may have a stronger effect than Dy on the hyperfine interaction anisotropies being discussed here.

We are not aware of a corresponding calculation for the case of the quadrupole interaction. The temperature variation of $\Delta\varepsilon$ looks qualitatively similar except that its maximum value increases with Dy concentration rather than decreasing.

5. Conclusions

Single crystals of the mixed rare-earth orthoferrite $Dy_{1-x}Ho_xFeO_3$ ($x = 0.25, 0.5,$ and 0.75) have been studied by Mössbauer spectroscopy in the 1.3–298 K temperature range. Several temperature-induced Fe^{3+} spin reorientation transitions have been observed, in qualitative agreement with previous neutron diffraction and magnetization measurements [11–13]. A reorientation from the a to the b orthorhombic axis took place near 40 K with an apparent width of the order of 10 K in most of the absorbers. The temperature variation of the relative line intensities in the Mössbauer spectra measured with (110)-plane absorbers shows that it is discontinuous locally.

Upon further cooling, the Fe^{3+} spins performed a continuous reorientation from the b to the c axis. The onset temperature of the latter transition depended linearly on Ho concentration x, in very good agreement with theoretical predictions [13].

The $x-T$ phase diagram of $Dy_{1-x}Ho_xFeO_3$ proposed here extrapolates well to the results of previous studies of pure $HoFeO_3$ and pure $DyFeO_3$.

The continuous Fe^{3+} spin rotation in the bc plane showed a marked differential anisotropy of hyperfine interactions of ^{57}Fe nuclei in positions 1, 3 and 2, 4. The temperature variation of the difference in magnetic hyperfine fields agrees very well with a previous calculation of a similar effect in NMR.

We also observed a new, very sharp Fe^{3+} spin reorientation between 3 and 2.3 K in a $Dy_{0.75}Ho_{0.25}FeO_3$ single-crystal absorber. We showed that it was a reverse reorientation from the c to the b orthorhombic axis upon cooling. This transition, which to the best of our knowledge has not been reported before, seems to be an analogue to the $\Gamma_2(Fe,Tb)-\Gamma_4(Fe)\Gamma_8(Tb)$ phase transition in $TbFeO_3$ below 4.2 K, which is driven by antiferromagnetic ordering of the rare-earth spin system. However, in the present case the lowest-temperature phase of the iron spin subsystem appears to be $\Gamma_1(G_y)$. Our suggestion for the rare-earth spin arrangement is $\Gamma_5(g_x a_y)$.

Acknowledgments

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