Magnetic Exchange Interactions in Perovskite Solid Solutions. Part 1. Iron-57 and ^{151}Eu Mössbauer Spectra of $EuFe_{1-x}Co_xO_3$ ($0 < x < 1$)

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The ^{151}Eu and ^{57}Fe resonances have been used to study magnetic exchange interactions in the orthorhombic perovskite solid solution $EuFe_{1-x}Co_xO_3$ ($0 < x < 1$). The replacement of a neighbouring Fe^{3+} ion by diamagnetic Co^{3+} ion results in a reduction in the flux density of the supertransferred hyperfine field at the ^{57}Fe nucleus of 1.02 ± 0.05 T extrapolated to 0 K. The ^{151}Eu resonance is considerably broadened by substitution; this effect is proved to be of magnetic origin, and a detailed model is proposed which explains the data quantitatively. The flux density of the molecular exchange field at the ^{151}Eu nucleus when a neighbouring Fe^{3+} atom is substituted by Co^{3+} is expressed by the exchange constant $(\beta/k)B_0^m(0) = 3.2 \pm 0.1$ K.

The rare-earth iron perovskites, ABO_3 (B = Fe), have been extensively studied by ^{57}Fe Mössbauer spectroscopy; the major features of the spectra are well illustrated in the comprehensive paper by Eibschutz *et al.*[1] Solid solutions have received less attention, although a detailed study by Nishihara[2] of $TbFe_{1-x}Cr_xO_3$ showed that nearest-neighbour effects could be resolved in the ^{57}Fe spectra and were partly attributed to supertransferred hyperfine interactions. The latter have also been seen at $^{119}Sn^{4+}$ impurity ions introduced into B-sites of perovskite solid solutions with charge-compensating Ca^{2+} ions at the rare-earth A-site.[3] Comparatively few data are available for europium perovskites despite the ease with which the ^{151}Eu Mössbauer resonance can be recorded. In a recent paper from this laboratory,[4] it was shown that the ^{151}Eu resonance in the orthorhombic perovskites $EuMO_3$ (M = Cr, Mn, Fe, or Co) is broadened by an unresolved quadrupole interaction with a coupling constant of e^2qQ_g *ca.* -6.5 mm s^{-1}. Although $EuCrO_3$ and $EuFeO_3$ are both essentially antiferromagnetic with only a weak ferromagnetism due to spin canting (Curie temperature, $T_c = 181$ and 662 K respectively), there is no evidence to suggest that the ^{151}Eu resonance is significantly broadened by any magnetic exchange interaction. This is fully consistent with the antiferromagnetic structure in which each Eu atom has eight M nearest-neighbour cations in mutually compensating pairs. In contrast it was found[5] that the ^{151}Eu resonance in antiferromagnetic $SrEu_2Fe_2O_7$ shows a significant magnetic hyperfine interaction; the Eu environment consists of only seven Fe nearest neighbours and thus compensation remains incomplete. Although it had been predicted[4] that random solid solutions with two metals on the B-site would show magnetic effects, preliminary data for $EuFe_{0.8}Cr_{0.2}O_3$ and $EuFe_{0.9}Al_{0.1}O_3$ suggested that these were much smaller than expected. It was difficult to be certain that the small broadening of the ^{151}Eu resonance which was found did not arise simply from quadrupole effects.

In this paper a study by ^{57}Fe and ^{151}Eu Mössbauer spectroscopy of the solid solution $EuFe_{1-x}Co_xO_3$ ($0 < x < 1$) is presented which conclusively demonstrates the existence of magnetic exchange interactions in the ^{151}Eu resonance. The data are interpreted with a detailed model which gives a quantitative estimate of the strength of the exchange.

Experimental

Samples in the solid solution $EuFe_{1-x}Co_xO_3$ were prepared for $x = 0$—1.0 in increments of 0.1 as follows. Accurately weighed samples of $K_3[Fe(CN)_6]$ and $K_3[Co(CN)_6]$ were dissolved in the minimum of hot distilled water and precipitated as the complex cyanide $Eu[M(CN)_6]\cdot xH_2O$ (M = Fe/Co mixture) with an excess of Eu_2O_3 just dissolved in concentrated HCl. In this way the stoicheiometry of europium to transition metal could be controlled. The precipitates were then filtered and calcined at 1 000 °C for 24 h to produce the perovskite. Preliminary *X*-ray analysis of some samples showed inhomogeneity, and all were subsequently refired to >1 200 °C for several days. It was not established whether the inhomogeneity resulted from the precipitation of mixed crystals, or from a phase separation during the decomposition. The final products were characterized by *X*-ray diffraction recorded with a Philips diffractometer using nickel-filtered Cu-K_α radiation. All samples gave patterns characteristic of the orthorhombic perovskite with no other phases evident. The parameters for $EuFeO_3$ and $EuCoO_3$ agreed well with published data. The lattice parameters *a*, *b*, *c*, and cell volume for the solid solutions showed a linear variation with composition, there being a total decrease of 2.2, 4.2, 2.7, and 8.9% respectively as Fe^{3+} is replaced by the smaller Co^{3+} ion.

The ^{57}Fe and ^{151}Eu spectra were obtained at various temperatures using established techniques and source matrices of ^{57}Co(Rh) and $^{151}SmF_3$ respectively. The data were analysed by digital computer using various theoretical models as described in the text.

Absorbers were made to a nominal thickness of 20 mg cm^{-2} of the perovskite by accurately weighing out the appropriate material, grinding with a large excess of MgO as a diluent and abrasive, and packing the mixture into an absorber holder. In this way all the absorbers used had approximately the same absorption cross-section for the ^{151}Eu resonance (but not for ^{57}Fe) so that comparisons of linewidth could be made in a meaningful way. From the results obtained, this procedure was clearly successful.

Results and Discussion

Crystal and Magnetic Structure of $EuFeO_3$.—The compound $EuFeO_3$ has been shown[6] to belong to the orthorhombic space group *Pbnm* (D_{2h}^{16}) with $a = 537.2$, $b = 560.6$, $c = 768.5$ pm, and $Z = 4$. The Eu^{3+} sites have the point symmetry *m* (C_s), and they lie in mirror planes which also contain oxygen anions and are normal to the *c* axis. There are 12 oxygen neighbours with Eu–O bond distances ranging from 229.7 to 351.0 pm, and eight nearest-neighbour iron sites in pairs (above and below the mirror plane) at 312.7, 325.7, 338.3, and 368.2 pm. The Eu–O–Fe bond angles are between 69.5 and 115.0°.

The structure is illustrated in Figure 1 as a projection onto the mirror plane; only those iron and oxygen atoms immediately above and below the mirror plane are shown. The

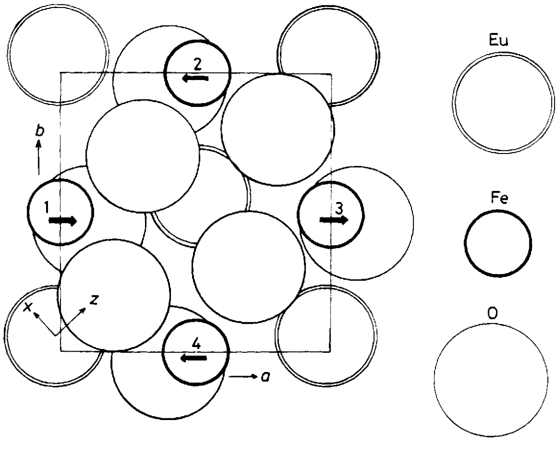

Figure 1. Projection of the structure of $EuFeO_3$ on the *ab* plane. The spin directions in the upper layer of Fe^{3+} ions are shown, those in the lower layer being reversed, and the numbers identify individual atoms referred to in the text. The axes of the e.f.g. tensor at the Eu^{3+} site are also shown

magnetic structure is well known.[7] The dominant iron–iron exchange interaction causes the Fe^{3+} spins to couple antiferromagnetically parallel to the *a* axis in a magnetic mode G_x. The spin directions for the upper layer of Fe atoms are shown in Figure 1 as solid arrows; those for the lower layer are reversed. This spin configuration is also symmetry compatible with the mode F_z, and consequently the spins are slightly canted to give a net ferromagnetic moment in the *c* direction. The canting angle in $EuFeO_3$ is only 8.0 mrad (0.46°), and is effectively independent of temperature.[1]

The $^7F_0$ ground state for Eu^{3+} ($4f^6$) is diamagnetic and does not give rise to an electric field gradient (e.f.g.). However, the $^7F_1$ and $^7F_2$ low-lying excited states can mix into the ground state if the crystalline field is non-cubic and result in a temperature dependent e.f.g. which is additional to the temperature-independent contribution from the external lattice charges. The calculation of the total e.f.g. in $EuFeO_3$ from the crystal structure data was given in full in the earlier paper.[4] The values at 4.2 K of $e^2qQ_g = -7.83$ mm s^{-1}, $\eta = 0.11$, V_{zz} at 42° to the *a* axis, and V_{yy} along the *c* axis were almost independent of temperature up to 300 K, although the value for e^2qQ_g does depend slightly on the numerical values used for the various shielding constants. However, agreement with the experimental value of $e^2qQ_g = -6.6$ mm s^{-1} in $EuFeO_3$ was considered to be satisfactory. The equivalent experimental value in $EuCoO_3$ was -6.5 mm s^{-1}.

The Solid Solution.—The Co^{3+} ion in $EuCoO_3$ is diamagtic at low temperatures and may be presumed to have the low-spin configuration t_{2g}^6 in the near octahedral co-ordination to oxygen.[8] There are indications that the high-spin $t_{2g}^4e_g^2$ configuration is partially populated at temperatures above 500 K.[8,9] The linear dependence of the lattice parameters on *x* in the solid solution $EuFe_{1-x}Co_xO_3$ is a good indication that the Co^{3+} ion has a low-spin diamagnetic ground state across the phase. A measurement of the magnetic susceptibility at room temperature for the sample with $x = 0.5$ supported this, but the magnetic properties have not been investigated in sufficient detail to provide full confirmation.

There have been several reports to the effect that a very small degree of substitution (0.25%) of iron with cobalt in $YFeO_3$ and $DyFeO_3$ can cause a reorientation of the Fe^{3+} spins. However, it is believed that this effect is due to long-range anisotropy effects of Co^{2+} ions associated with F^- impurities.[10-12] The possibility of spin-reorientation effects in $EuFe_{1-x}Co_xO_3$ must therefore be borne in mind; the iron spins do not necessarily remain along the *a* axis.

The Curie temperature of $EuFeO_3$ is 662 K. Substitution of iron by a diamagnetic ion will weaken the exchange interactions and reduce the Curie temperature. The probability that a given Fe has *n* Co^{3+} neighbours in the first B-cation co-ordination sphere is given by equation (1).

$$p(n) = \frac{6!(1 - x)^{6-n}x^n}{(6 - n)!n!} \qquad (1)$$

If a given Fe is linked to only 0 or 1 other Fe atoms then it may be presumed not to participate in long-range magnetic order. Using the method of Gilleo,[13] it can be shown that the Curie temperature, T_c, has a compositional dependence shown by equation (2).

$$T_c(x) = (1 - x)(1 - 6x^5 + 5x^6)T_c(0) \qquad (2)$$

The Curie temperatures of the iron-rich samples were obtained to an accuracy of *ca.* ±5 K by observing the collapse of magnetic hyperfine structure in a series of ^{57}Fe Mössbauer spectra. The results (theory in parentheses) are shown below.

x	T_c/K
0.1	605 (596)
0.2	524 (529)
0.3	439 (458)
0.4	405 (381)
0.5	234 (295)
0.6	<85 (203)

The experimental values are in reasonable accord with prediction for $x < 0.4$, but for $x > 0.4$ the Curie temperature falls off rapidly as the long-range magnetic continuity through the lattice is destroyed. These results are also in accord with a diamagnetic Co^{3+} ion.

^{57}Fe *Mössbauer Spectra.*—Magnetic hyperfine interactions were observed in the ^{57}Fe Mössbauer spectrum at 295 K (for $x \leqslant 0.4$) and at 85 K (for $x \leqslant 0.5$), with some additional spectra at other temperatures. The spectra for pure $EuFeO_3$ comprised a single six-line hyperfine pattern and were in agreement with published data.[1] The magnetic flux density was 50.8 T at 295 K and 55.5 T at 85 K. These values were calibrated using a value for iron metal of 33.0 T at 295 K. Because of the high Curie temperature, the value of the flux density at 85 K will be within 0.2 T of its saturation value at 0 K.

The quadrupole interaction is very small and is seen as a perturbation on the line positions with ε *ca.* 0.01 mm s^{-1} at 295 K. Because of its small magnitude, ε can be affected by systematic errors such as drive non-linearity, and is unfortunately not suitable for an unambiguous observation of spin-reorientation effects. This problem is compounded in the solid solutions where there are several overlapping components, and although there was evidence to suggest that ε changed sign for $x = 0.1$ and 0.2 at 85 K, it would be unwise to assume that these observations were significant.

Quadrupole interactions can be seen clearly in the absence of magnetic splitting; for example, when $x = 0.5$ the spectrum at 295 K is a resolved doublet with a splitting of 0.38 mm s^{-1}. The small value of ε is clearly the result of the orientation of the principal axis of the e.f.g. at *ca.* 45° to the magnetic spin axis.

The spectrum at 295 K for $EuFe_{0.9}Co_{0.1}O_3$ is shown in Figure 2, and one of the outer lines on an expanded scale is shown in Figure 3. The three components which can be dis-

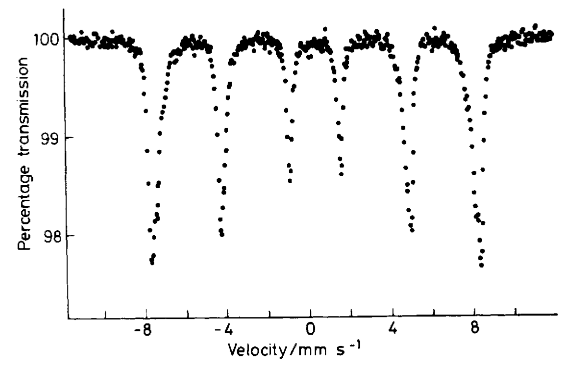

Figure 2. The ^{57}Fe Mössbauer spectrum of $EuFe_{0.9}Co_{0.1}O_3$ at 295 K. Note the inward broadening of the resonance lines, an effect which increases substantially as x increases

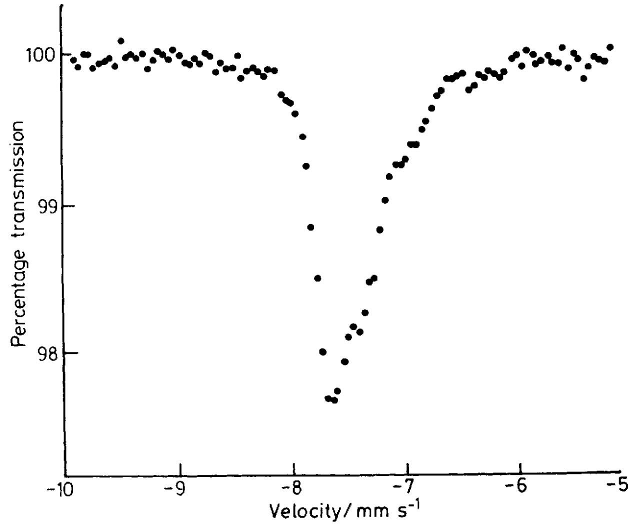

Figure 3. One of the outer lines in Figure 2 on an expanded scale. The three partially resolved components of the line from left to right are attributable to Fe^{3+} sites with a 6 Fe^{3+} neighbours (53%), 1 Co^{3+} and 5 Fe^{3+} neighbours (35%), and 2 Co^{3+} and 4 Fe^{3+} neighbours (10%)

cerned in Figure 3 are (from left to right) attributable to Fe^{3+} sites with 6 Fe^{3+} neighbours (53%), 1 Co^{3+} and 5 Fe^{3+} neighbours (35%), and 2 Co^{3+} and 4 Fe^{3+} neighbours (10%) respectively. This behaviour has already been found in many solid solutions,[2] and is a combination of two effects. First, the magnetisation and hence the flux density at any given site show a temperature dependence which is a function of the near-neighbour environment and can be fully interpreted [14] using molecular-field theory; in general a substituted environment leads to a decrease in the field. Secondly, the flux density extrapolated to 0 K reaches a different limiting value for each near-neighbour environment because of the supertransferred hyperfine contribution to the flux density. The supertransferred hyperfine field (s.t.h.f.) at the nucleus is produced by the 3*d* spins of neighbouring magnetic cations, and is therefore affected by substitution.[15] The antiparallel spin of the six Fe^{3+} neighbours ($S = \frac{5}{2}$) results in the s.t.h.f. and the intrinsic hyperfine field being additive. Substitution by another magnetic ion will normally reduce the total s.t.h.f. and result in a decrease in flux density. It is usually considered that only the first neighbour spins are important, but there may well be a small contribution from more distant spins which is not readily distinguished.

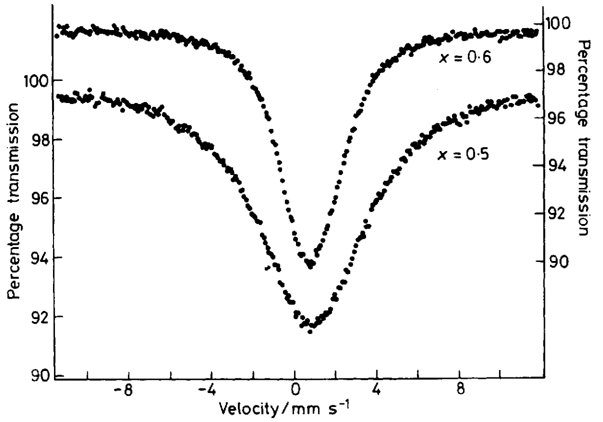

Figure 4. The ^{151}Eu Mössbauer spectra at 85 K for $EuFe_{0.5}Co_{0.5}O_3$ and $EuFe_{0.4}Co_{0.6}O_3$. Note the broader resonance for the former ($x = 0.5$) which has a Curie temperature of *ca.* 234 K compared to the latter ($x = 0.6$) which is paramagnetic

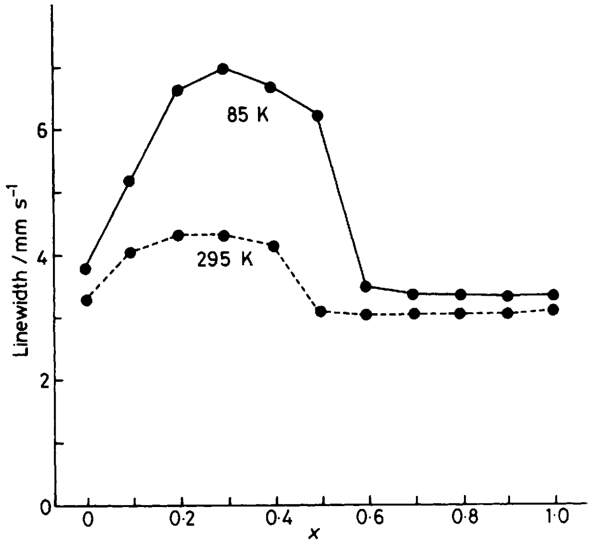

Figure 5. The linewidth at half-height for the ^{151}Eu spectra fitted with a single Lorentzian lineshape as a function of the composition x. The data values are shown as full circles and the solid and dashed lines are cosmetic without functional significance

In the present instance the ^{57}Fe spectra at room temperature show good resolution of near-neighbour environments, and although the molecular field and s.t.h.f. contributions are not separable, these spectra serve to verify the composition and randomness of the solid solutions. However, for $x < 0.3$ the spectra at 85 K are close to saturation and allow a direct determination of the s.t.h.f. It should be noted that the iron site is at an inversion centre, so that there are three pairs of distinct Fe–O–Fe exchange interactions. However, the Fe–O bond distances (200.0, 201.0, and 202.9 pm) and Fe–O–Fe angles (147.8 and 148.0°) in $EuFeO_3$ are closely comparable. Therefore to a first approximation all six exchange interactions can be considered equal, and it is assumed that the change in s.t.h.f. when Fe is replaced by Co is the same for all six neighbouring sites. This approximation is consistent with the observed component intensities in the spectra.

It is difficult to be certain that the change in the flux density of the s.t.h.f., ΔB, which is observed when Co replaces Fe is a linear function of the number of atoms substituted. Fitting a number of independent fields with the same linewidth and quadrupole perturbation, and with intensities constrained only by the binomial populations for a random solid solution seemed to suggest that ΔB increased slightly with n, but this may have been an artefact of the calculation which unavoidably neglected weak inner components. In the event it was found that good computer fits could be obtained by including all components for which $p(n) > 0.01$ with a field distribution given by $B - n\Delta B$, *i.e.* with a constant value for the change in s.t.h.f. The computed values obtained from the spectra at 85 K were $B = 55.23 \pm 0.01$ and $\Delta B = 1.02 \pm 0.01$ T for $x = 0.1$, and $B = 54.75 \pm 0.02$ and $\Delta B = 1.03 \pm 0.01$ T for $x = 0.2$. Thus the s.t.h.f. for replacement of Fe^{3+} by Co^{3+} can be taken as $\Delta B = 1.02 \pm 0.05$ T.

This value will be discussed further with respect to s.t.h.f. values for other substituent atoms in a later paper.

^{151}Eu *Mössbauer Spectra.*—The ^{151}Eu Mössbauer resonance was measured at 85 and 295 K for all samples at a constant thickness of 20 mg cm^{-2}, and in each case was found to comprise a single broad line without resolved fine structure, although the narrowest lines were slightly asymmetric. Some typical spectra are shown in Figure 4. As a first analysis, all spectra were curve-fitted with a single Lorentzian lineshape, and the values for the linewidth at half-height are shown in Figure 5. At 295 K, the samples with $x > 0.5$ and $EuFeO_3$ itself gave computed linewidths of *ca.* 3 mm s^{-1}. For the substituted samples below their Curie temperatures ($0.1 \leqslant x \leqslant 0.4$), the linewidth was substantially larger (>4 mm s^{-1}) although remarkably the lineshape was even closer to Lorentzian in character. At 85 K this difference was greatly accentuated with the additional observation that broadening was now seen for $x = 0.5$ ($T_c = 234$ K).

Two observations can be made. First, the constant linewidth in the paramagnetic samples shows that replacement of Fe by Co does not produce any additional broadening of quadrupolar origin. Secondly, the increased linewidth in solid solutions below their Curie temperatures is clearly of magnetic origin. The slightly greater linewidth in $EuFeO_3$ as compared to $EuCoO_3$ may reflect the ferromagnetic component in the former, although as predicted the difference is small.

The spectrum at 295 K for $x = 0.5$ was curve-fitted with a quadrupole pattern equivalent to that for pure $EuFeO_3$,[4] and resulted in the parameters $e^2qQ_g = -6.79 \pm 0.09$ mm s^{-1}, $\eta = 0.81 \pm 0.03$, and linewidth $\Gamma = 2.17 \pm 0.03$ mm s^{-1}. These values were then used to investigate the magnitude of the magnetic interaction.

Model for the ^{151}Eu *Magnetic Interaction.*—As can be seen from Figure 1, each Eu site will experience the magnetic exchange fields from four equivalent pairs of Fe sites. The exchange interaction can only take place by direct cation–cation overlap or indirectly *via* the oxygen, the Fe–O–Eu bond angles ranging from 74.1 to 115.0°. In pure $EuFeO_3$ the exchange fields of pairs of crystallographically identical Fe spins mutually cancel because of the antiferromagnetic spin arrangement (except for the small ferromagnetic component). Therefore the Eu atom in $EuFeO_3$ does not experience an exchange field of any significant magnitude. On the other hand, if one ion in an equivalent pair is substituted, then a substantial exchange field will result. In the earlier paper [4] it was remarked that for $x = 0.2$, 17% of the sites have no cobalt neighbours (and therefore no exchange field), but that 83% of the sites will experience an imbalance in the exchange interaction. This is not valid, because some of the substituted pairs will also be opposed to each other, and the correct statistical treatment is more complex.

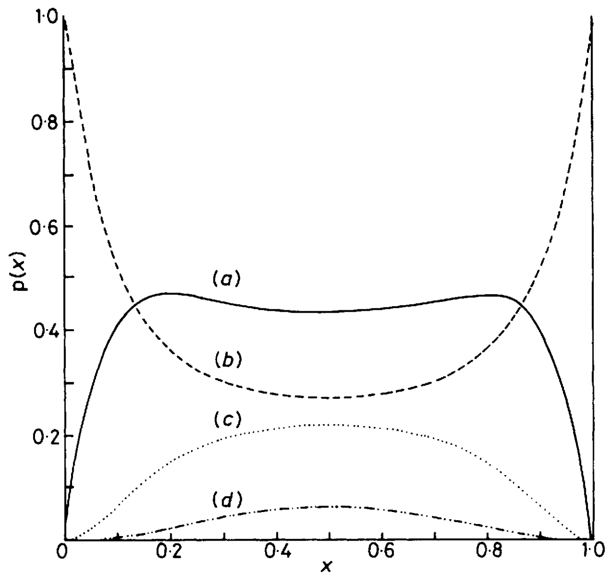

Figure 6. The probability p(x) as a function of composition x that the flux density of the molecular exchange field $|B^m|$ will be a particular multiple of $B_0{}^m$. $|B^m| = B_0{}^m$ (*a*), zero (*b*), $2B_0{}^m$ (*c*), and $3B_0{}^m$ (*d*). The curve for $4B_0{}^m$ is omitted because it lies very close to the baseline

Let us simplify the argument by assuming that all eight Fe sites are magnetically equivalent in their effect at the Eu site apart from a choice of spin direction. If an Fe atom gives a molecular exchange field at the Eu site with a flux density of B_1, and the Co atom similarly gives a flux density of B_2, then the probability of a zero resultant from a given pair of Fe sites with antiparallel spin alignment is $1-2x + 2x^2 = a$ (*i.e.* 0 or 2 Fe atoms); for a resultant field of $B_1 - B_2$ the probability is $x(1 - x) = b$, and of $B_2 - B_1$ is also $x(1 - x)$. Combining together all eight spins about the Eu site to calculate the flux density of the total molecular exchange field, B^m, in multiples of $B_0{}^m = |B_1 - B_2|$, the results are shown below.

$\|B^m\|$	probability, p(x)
0	$a^4 + 12a^2b^2 + 6b^4$
$B_0{}^m$	$8a^3b + 24ab^3$
$2B_0{}^m$	$12a^2b^2 + 8b^4$
$3B_0{}^m$	$8ab^3$
$4B_0{}^m$	$2a^4$

It now follows that for $x = 0.2$, 36% of the sites experience a negligible exchange field, and 46% are effectively influenced by only one uncompensated spin with an exchange field corresponding to $B_0{}^m$. This also explains why the magnetic broadening in the substituted perovskites is small. In the real case where all the spins are not equivalent, then there will be a spread of values of B^m, but to a first approximation this simplified model should be adequate. There is also the possibility that there is a small contribution from second- and third-neighbour cations, but this has also been neglected.

The relationship between the flux density of the molecular exchange field B^m and the observed hyperfine flux density B has been treated in great detail elsewhere.[4] It is effectively linear for the values experienced in the present instance. The spectrum recorded comprises a number of magnetically broadened resonances with flux densities of 0, B, $2B$, $3B$, and $4B$, and with weights p(x) given by the above expressions. The composition dependence of p(x) is illustrated in Figure 6, and shows that remarkably little compositional dependence is displayed for $0.2 < x < 0.8$. It is convenient to express the molecular exchange field directly in thermal energy units (K)

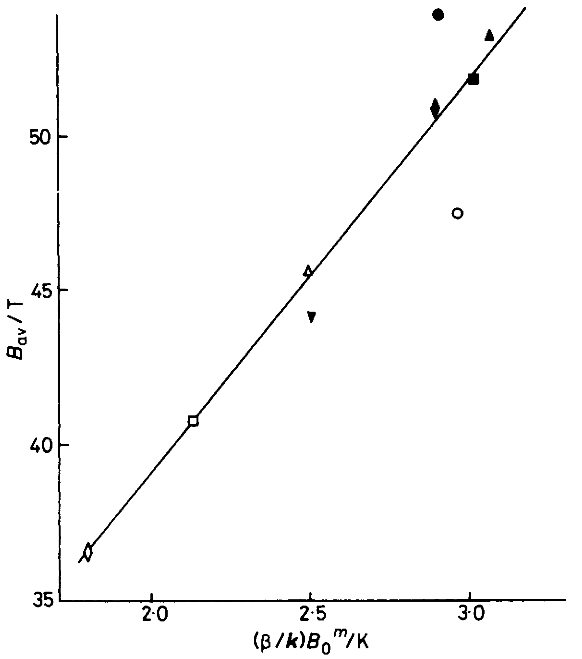

Figure 7. The mean flux density for ^{57}Fe with one or more Co neighbours, B_{av}, plotted against the flux density of the ^{151}Eu molecular exchange field, $(\beta/k)B_0{}^m$. Data points at 85 K are shown as filled symbols, data at 295 K as open symbols: $x = 1$ (○,●), 0.2 (△,▲), 0.3 (□,■), 0.4 (◇,◆), and 0.5 (▼). The saturation limit for B_{av} is 54.0 T

as an exchange constant, $(\beta/k)B^m$ (β is the Bohr magneton, k Boltzmann's constant).

Interpretation of ^{151}Eu *Data*.—The ^{151}Eu spectra were computer analysed using a model in which five magnetic hyperfine components were assumed to exist as described in the preceding section. The quadrupole parameters were fixed at those deduced for $x = 0.5$ at 295 K, and the relative orientations of the e.f.g. tensor and the spin axis were fixed from the earlier e.f.g. calculations[4] assuming the spins to lie along the a axis. In this way an experimental value for $B_0{}^m$ could be deduced. Thus at 85 K for $x = 0.2$ the effective flux density $B_{eff.}$ is 7.32 ± 0.11 T, leading to a value for $(\beta/k)B_0{}^m$ of 3.07 ± 0.05 K. Since the Co^{3+} ion is diamagnetic, the magnitude of $B_0{}^m$ will be proportional to the magnetisation of the Fe^{3+} ion and hence the magnetic flux density at the ^{57}Fe nucleus. It should be noted that Fe atoms with no Co neighbours *cannot* contribute to the observed value for $B_0{}^m$. Accordingly, the values of $B_0{}^m$ deduced from samples of different composition at both 85 and 295 K are plotted in Figure 7 against the mean flux density, B_{av}, at ^{57}Fe with one or more Co neighbours. As expected, there is a good correlation. Bearing in mind that Figure 7 includes data for $0.1 \leqslant x \leqslant 0.5$ and T = 85 and 295 K, the data treatment can be seen to be successful. The poorest agreement is for $x = 0.1$, at which composition the line broadening is considerably reduced with 51% of the sites in zero exchange field.

The possibility that the Fe spins reorientate to a different axis in the solid solution was also considered. A reorientation to the b axis has only a very small effect as the V_{zz} axis of the e.f.g. nearly bisects the angle between a and b. A reorientation to the c axis would result in an overestimation of $B_0{}^m$ by *ca.* 15%. In the absence of any positive evidence for a change in spin axis, it is assumed that the spins remain aligned along the a axis.

Table. Bond parameters in EuFeO$_3$

Fe	Eu–Fe/pm	Fe–O/pm	Eu–O/pm	Fe–O–Eu/°
1	338.3	200.0	229.7	103.7
		201.0	269.2	90.8
		202.9	351.0	69.5
2	312.7	200.0	236.5	91.1
		201.0	256.1	85.4
		202.9	269.2	81.7
3	325.7	201.0	233.1	96.9
		202.9	256.1	89.6
		200.0	317.6	74.1
4	368.2	202.9	233.1	115.0
		200.0	337.4	82.2
		201.0	351.0	78.5

The data in Figure 7 can be extrapolated to an average flux density of B_{av} = 54.0 T, corresponding to the T = 0 K limit for Fe^{3+} with 1 Co^{3+} neighbour, thus giving a zero-temperature value for the exchange constant of $(\beta/k)B_0{}^m(0) = 3.2 \pm 0.1$ K. This value is an averaged ' effective ' parameter for an octahedral site Fe^{3+} ion with an Fe–O–Eu angle of *ca.* 90°. It can be compared to the value of $(\beta/k)B_0{}^m(0) = 3.0$ K found in Sr$_2$Eu$_2$Fe$_2$O$_7$ where the Fe–O–Eu angle is 154°. In the latter compound the exchange takes place through only one oxygen. In the orthorhombic perovskites this may still be effectively the case, because although each Fe connects to Eu through three oxygens, some of the Eu–O distances are quite long. As can be seen from the Table, there may be only one strong exchange path per iron with a bond angle ranging from 91 to 115°. One may therefore conclude either that the Eu–O–Fe exchange is not strongly dependent on bond angle, or that the slightly longer Fe–O bond length in Sr$_2$Eu$_2$Fe$_2$O$_7$ of 224 pm has significantly weakened the exchange. The latter is consistent with the case of Eu$_3$Fe$_5$O$_{12}$ where the exchange constant of $(\beta/k)B_0{}^m(0) = 26$ K *via* two equivalent Fe–O bonds of 188 pm in tetrahedral co-ordination is very large despite the low Eu–O–Fe bond angle of 92°.

Further discussion of the exchange interactions will be deferred until work is completed on solid solutions with a range of other magnetic and non-magnetic M^{3+} cations.

Acknowledgements

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References

1 M. Eibschutz, D. Shtrikman, and D. Treves, *Phys. Rev.*, 1967, **156**, 562.
2 Y. Nishihara, *J. Phys. Soc. Jpn.*, 1975, **38**, 710.
3 A. S. Moskvin, N. S. Ovanesyan, and V. A. Trukhtanov, *Hyperfine Interactions*, 1977, **5**, 13.
4 T. C. Gibb, *J. Chem. Soc., Dalton Trans.*, 1981, 2245.
5 T. C. Gibb, *J. Phys. C.*, 1981, **14**, 1985.
6 M. Marezio, J. P. Remeika, and P. D. Dernier, *Acta Crystallogr., Sect. B*, 1970, **26**, 2008.
7 R. L. White, *J. Appl. Phys.*, 1969, **40**, 1061.
8 A. Kappatsch, S. Quezel-Ambrunaz, and J. Sivardière, *J. Phys. (Paris)*, 1970, **31**, 369.
9 V. G. Jadhao, R. M. Singru, G. N. Rao, D. Bahadur, and C. N. R. Rao, *J. Phys. Chem. Solids*, 1976, **37**, 113.
10 K. P. Belov, A. K. Gapeev, A. M. Kadomtseva, T. M. Ledneva, M. M. Lukina, T. L. Ovchinnikova, and N. A. Khafizova, *Sov. Phys. Solid State*, 1974, **15**, 1501.

11 Yu. S. Vishnyakov, L. G. Lyubutina, and I. S. Lyubutin, *Sov. Phys. Solid State*, 1975, **17**, 409.

12 O. N. Nickolev, T. H. Ruskov, S. A. Georgiev, A. M. Kadomtseva, I. B. Krinetsteii, M. M. Lukina, and N. V. Bazhanova, *J. Magn. Mater.*, 1980, **22**, 15.

13 M. A. Gilleo, *J. Phys. Chem. Solids*, 1960, **13**, 33.

14 J. M. D. Coey and G. A. Sawatzky, *Phys. Status. Solidi B*, 1971, **44**, 673.

15 M. A. Butler, M. Eibschutz, and L. G. Van Uitert, *Solid State Commun.*, 1973, **12**, 499.

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