Magnetic Exchange Interactions in Perovskite Solid Solutions. Part 2.[1] Iron-57 and ^{151}Eu Mössbauer Spectra of $EuFe_{1-x}Cr_xO_3$ ($0 < x < 1$)

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The ^{151}Eu and ^{57}Fe Mössbauer resonances have been used to study magnetic exchange interactions in the orthorhombic perovskite solid solution $EuFe_{1-x}Cr_xO_3$ ($0 < x < 1$). The supertransferred hyperfine field (s.t.h.f.) at ^{57}Fe due to a Cr^{3+} nearest-neighbour cation has the same sign as that due to Fe^{3+}, and the observed reduction in the flux density of the s.t.h.f. when Cr^{3+} replaces Fe^{3+} is 0.82 ± 0.02 T extrapolated to 0 K. The flux density of the molecular exchange field at Eu^{3+} due to a Cr^{3+} ion has the same sign as that due to Fe^{3+}.

Recent work in this laboratory[2] has shown that the ^{151}Eu Mössbauer 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 both $EuCrO_3$ and $EuFeO_3$ are basically antiferromagnetic with only a weak ferromagnetism due to spin canting ($T_c = 181$ and 662 K respectively), the ^{151}Eu resonance is not significantly broadened by any magnetic exchange interaction. The antiferromagnetic arrangement of the spins is such that each Eu atom has eight M nearest-neighbour cations in mutually compensating pairs. Subsequently, a detailed investigation of the solid solution $EuFe_{1-x}Co_xO_3$ ($0 < x < 1$) conclusively demonstrated the existence of magnetic exchange interactions in the ^{151}Eu resonance, and a quantitative interpretation was developed.[1]

In this paper similar measurements are reported for the solid solution $EuFe_{1-x}Cr_xO_3$. This is a particularly interesting solid solution because both transition-metal cations have a magnetic moment and the end members of the phase, $EuFeO_3$ and $EuCrO_3$, have an identical magnetic structure with an antiferromagnetic M–O–M superexchange. However, it is not immediately obvious as to whether the Fe–O–Cr superexchange in the solid solution is antiferromagnetic or ferromagnetic, and considerable controversy has arisen over this particular aspect. The results reported here were initiated as part of an attempt to resolve this problem.

Experimental

Samples in the solid solution $EuFe_{1-x}Cr_xO_3$ were prepared for $x = 0$—1.0 in increments of 0.1 as follows. Accurately weighed samples of high-purity Eu_2O_3, Fe_2O_3, and Cr_2O_3 were ground together in a ball-mill and fired in air to *ca.* 1 300 °C for 3—4 d. For reasons detailed later, the samples were then reground and refired at least twice for a total time of 12—16 d. The best results were obtained with a small initial excess of Eu_2O_3 to allow for evaporation. The solid solutions were characterised 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 lattice parameters *a*, *b*, *c*, and cell volume showed a linear variation with composition, there being a total decrease of 0.6, 1.9, 0.9, and 3.3% respectively as Fe^{3+} is replaced by the smaller Cr^{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 as described in the text.

Absorbers were made with approximately the same absorption cross-section for the ^{151}Eu resonance (but not for ^{57}Fe) by accurately weighing out 20 mg cm^{-2} of the perovskite, grinding with an excess of MgO, and packing uniformly into an absorber holder. This technique had already been used successfully for the $EuFe_{1-x}Co_xO_3$ experiments.

Results and Discussion

Structural Characteristics of the Phase.—Although both $EuFeO_3$ and $EuCrO_3$ belong to the orthorhombic space group *Pbnm* (D_{2h}^{16}), accurate atomic co-ordinates are only available for the former.[3] The relevant features of the structure have been illustrated and discussed in Part 1 of this series,[1] and only a short resumé is given here. The Eu^{3+} sites lie in mirror planes with eight nearest-neighbour iron sites in four pairs above and below the mirror plane at distances of 312.7, 325.7, 338.3, and 368.2 pm, and with Fe–O–Eu bond angles in the range 69.5—115.0°. The FeO_6 polyhedra are close to regular octahedral, and the average Fe–O–Fe bond angle is 148°. In the magnetically ordered phase the iron moments lie parallel to the *a* axis in a magnetic mode referred to as G_x, and pairs of equivalent iron atoms related by the mirror plane are antiferromagnetically aligned. The spin canting is so small as to be negligible for the present purposes. The low symmetry of the Eu^{3+} site causes mixing of the $^7F_0$ ground state with the low-lying $^7F_1$ and $^7F_2$ excited states, and the resulting electric field gradient causes a substantial quadrupolar broadening of the ^{151}Eu Mössbauer resonance which has been evaluated in detail.[2]

The compound $EuCrO_3$ has very similar lattice parameters and the same magnetic structure, and it is generally assumed that the bond distances and bond angles are very close to the values in $EuFeO_3$.

The Curie temperatures of the iron-rich samples were obtained to an accuracy of about ±5 K by observing the collapse of magnetic hyperfine structure in a series of ^{57}Fe Mössbauer spectra. The results are shown below with the corresponding theoretical figure for substitution by a diamagnetic cation in parentheses.

x	T_c/K
0	622
0.1	572 (595)
0.2	497 (529)
0.3	415 (458)
0.4	330 (381)
0.5	234 (295)
0.6	185 (203)

The T_c values for cobalt substitution with $x < 0.5$ (t_{2g}^6, $S = 0$) were in reasonable agreement with theoretical prediction for substitution by a diamagnetic cation,[1] but the corresponding T_c values for chromium substitution (t_{2g}^3, $S =$

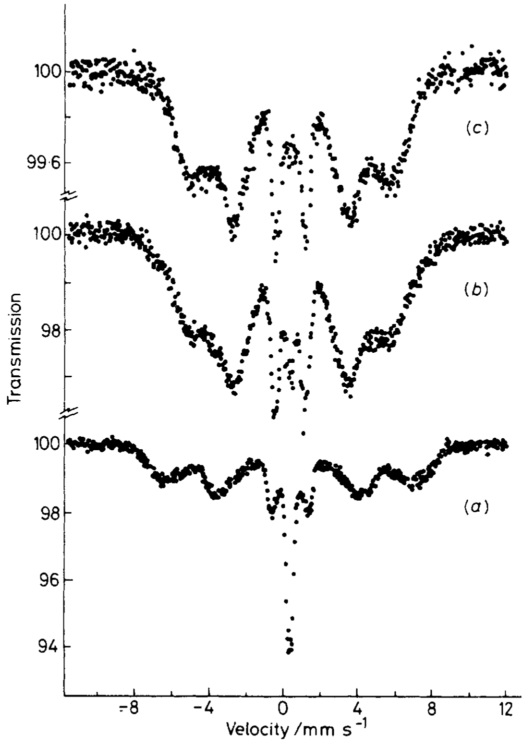

Figure 1. The ^{57}Fe Mössbauer spectra at 295 K of a solid solution with nominal composition $EuFe_{0.6}Cr_{0.4}O_3$ after (*a*) firing at 1 260 °C for 4 d, (*b*) regrinding and firing to 1 345 °C for 6 d, and (*c*) a second regrinding and firing to 1 100 °C for 3 d followed by 1 380 °C for 5 d

$\frac{3}{2}$) are anomalously low, and for $x > 0.6$ approach the limiting value of $T_c = 181$ K for pure $EuCrO_3$. Similar behaviour has been recorded independently for $TbFe_{1-x}Cr_xO_3$ by Nishihara.[4] The approximations of Hashimoto,[5] which use molecular field theory to predict the Curie temperature of a solid solution as a function of x and the exchange constant J(Fe–Cr), predict that for $x < 0.5$ the value of T_c should be close to or greater than that for diamagnetic substitution, and are unable to reproduce the behaviour observed. In any case, it should be noted that the molecular field theory approach can only determine the modulus $|J(\text{Fe–Cr})|$, and the sign of the interaction is not indicated.

^{57}Fe *Mössbauer Spectra.*—The ^{57}Fe Mössbauer spectra were recorded at 295 and 85 K for samples with $x < 0.7$. At an early stage it was realised that a sample which showed a single-phase perovskite *X*-ray pattern did not necessarily have a fully randomised distribution of Fe^{3+} and Cr^{3+} ions. In Figure 1 are shown the ^{57}Fe spectra at 295 K for a sample with $x = 0.4$ after (*a*) firing at 1 260 °C for 4 d, (*b*) regrinding and further firing at 1 345 °C for 6 d, and (*c*) a second regrinding and firing to 1 100 °C for 3 d followed by 1 380 °C for 5 d. Although sample (*c*) gave marginally narrower lines in the *X*-ray powder pattern than sample (*a*), this effect could easily have been overlooked. It is fortuitous that the Curie temperature of 330 K for sample (*c*) is such that the iron magnetisation at 295 K lies on the steeply descending region of the Brillouin curve; the result is a marked sensitivity to the exact value of x and hence to any inhomogeneity in the sample. This effect has been recorded elsewhere[6] in incompletely annealed solid solutions of Fe_2O_3–Cr_2O_3 and Fe_2O_3–Al_2O_3.

In the present instance, the spectrum of (*c*) could be analysed satisfactorily by including hyperfine components from Fe atoms with zero, one, two, three, and four Cr neighbours and weighted with the binomial coefficients appropriate to a random solid solution. These results were then used as a criterion that the other samples in the phase received at least an equivalent heat treatment to ensure homogeneity.

The spectrum for pure $EuFeO_3$ comprised a single hyperfine pattern with a magnetic flux density of 50.8 T at 295 K and 55.5 T at 85 K. The value at 85 K will be within 0.2 T of the saturation value at 0 K because of the high Curie temperature of 662 K. The quadrupole interaction is seen as a very small perturbation of the line positions with ε *ca.* 0.01 mm s^{-1} at 295 K. This parameter had a similar value for $x = 0.1$ and 0.2 at both 295 and 85 K, and did not change sign at 85 K as it did in the cobalt-substituted samples.[1] Although one could suggest that this implies a spin reorientation in the cobalt phase (see ref. 1 for a detailed discussion), it is also possible that the same effect could be caused by a comparatively minor change in the electric field gradient tensor with temperature without any spin reorientation, and in the absence of further evidence this aspect will not be considered further.

Detailed analyses of the spectra were carried out using the same methods already described for the cobalt phase.[1] At 295 K the outer components of the spectra were seen to be broadened inwards as a result of additional hyperfine components which could be attributed to Fe^{3+} sites with six Fe^{3+} neighbours, five Fe^{3+} and one Cr^{3+}, four Fe^{3+} and two Cr^{3+}, *etc.* The probability of any given site environment was calculated from the usual binomial expression. As with cobalt substitution, a chromium-substituted environment leads to a decrease in the magnetic hyperfine field. At 295 K this is mainly due to a different temperature dependence of the iron magnetisation and is fully consistent with molecular field theory.[7] The different iron environments are easily distinguished in the spectra, and the relative intensities of the different hyperfine components provide a convenient check on the integrity of the solid solutions.

However, the flux density at 85 K, which for small x is very close to saturation so that the former effect is negligible, is nevertheless still dependent on substitution as a result of the supertransferred hyperfine field (s.t.h.f.) at the nucleus produced by the 3*d* spins of neighbouring magnetic cations.[8] In pure $EuFeO_3$ the antiparallel spins of the Fe^{3+} nearest neighbours result in the s.t.h.f. and the intrinsic magnetic hyperfine field of the Fe^{3+} ($S = \frac{5}{2}$) ion under observation being additive. Substitution by another magnetic ion usually produces a smaller s.t.h.f. and thereby causes a decrease in the flux density observed. Contributions from other than the nearest-neighbour spins are expected to be negligible. The s.t.h.f. effects are small but measurable. Following the procedure used for $EuFe_{1-x}Co_xO_3$, it was assumed that the change in the flux density of the s.t.h.f. is a linear function of the number of nearest neighbours substituted n, *i.e.* the observed flux density is given by $B - n\Delta B$. The computed values at 85 K were $B = 55.12 \pm 0.02$ T and $\Delta B = 0.81 \pm 0.02$ T for $x = 0.1$, and $B = 54.64 \pm 0.02$ T, and $\Delta B = 0.83 \pm 0.02$ T for $x = 0.2$. Thus the s.t.h.f. for replacement of Fe^{3+} by Cr^{3+} can be taken as $\Delta B = 0.82 \pm 0.02$ T.

This value for ΔB is substantially smaller than that found for Fe^{3+}/Co^{3+} (1.02 ± 0.05 T), but agrees well with the result of $\Delta B = 0.86 \pm 0.05$ obtained for $TbFe_{1-x}Cr_xO_3$ by Nishihara.[4] However, it seems that he may have been deceived into thinking that the s.t.h.f. due to Cr^{3+} could not be detected by this method from the similar value of $\Delta B = 0.91 \pm 0.05$ obtained from $TbFe_{1-x}Al_xO_3$. Duplicate spectra at 78 K were obtained to confirm that ΔB is indeed smaller for Cr^{3+} than for Co^{3+}. Diamagnetic Co^{3+} should produce no direct s.t.h.f., so that the smaller value of ΔB for Cr^{3+} suggests that the s.t.h.f. due to Cr^{3+} *has the same sign* as that from Fe^{3+}.

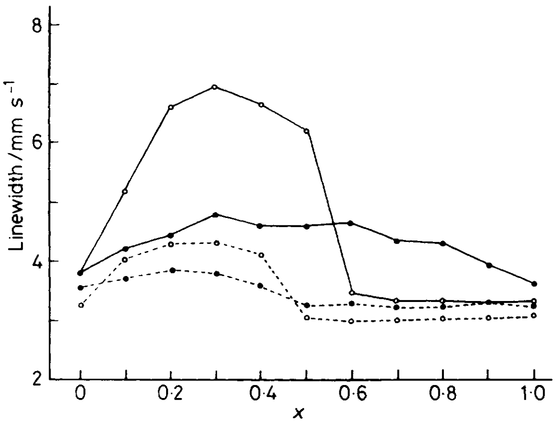

Figure 2. The linewidth at half-height for the ^{151}Eu spectra fitted with a single Lorentzian lineshape as a function of the composition x. The data values are shown as open circles (Co^{3+} substitution) or closed circles (Cr^{3+}), and the solid (85 K) and dashed lines (295 K) are cosmetic without functional significance

In principle this enables the sign of the Fe^{3+}–O–Cr^{3+} exchange to be determined, but a detailed discussion of this point will be deferred until Part 4 of this series, where other evidence will also be taken into consideration.

^{151}Eu *Mössbauer Spectra*.—The ^{151}Eu Mössbauer resonance was observed at 85 and 295 K for all samples at a constant thickness of 20 mg cm^{-2} to give effectively a constant cross-section for ^{151}Eu. In each case the spectrum comprised a single broad line without resolved fine structure, but the narrowest lines were slightly asymmetric. From the linewidths it was immediately apparent that the magnetic exchange in $EuFe_{1-x}Cr_xO_3$ was substantially weaker than in $EuFe_{1-x}Co_xO_3$. Numerical values of the linewidths obtained by curve-fitting a single Lorentzian profile are shown in Figure 2 for both phases. At 295 K the substituted phases with $x \leqslant 0.4$ are all below their respective Curie temperatures and give broader lines than phases with $x \geqslant 0.5$ which are paramagnetic. The constant linewidth for the latter verifies that replacement of Fe^{3+} by Cr^{3+} does not produce any additional broadening of quadrupolar origin. Magnetic exchange broadening is seen at 85 K for $x \leqslant 0.5$ in the cobalt phase and for all substituted samples in the chromium phase.

The spectrum at 295 K for $EuFe_{0.5}Cr_{0.5}O_3$ was curve-fitted with a quadrupole pattern [1,2] and gave the values for the coupling constant $e^2qQ_g = -7.23 \pm 0.08$ mm s^{-1}, asymmetry parameter $\eta = 0.71 \pm 0.02$, and linewidth $\Gamma = 2.34 \pm 0.02$ mm s^{-1}, and these values were assumed to specify the quadrupole interaction in the magnetic phases.

The magnetic exchange interaction was then evaluated using the model applied successfully to the $EuFe_{1-x}Co_xO_3$ phase.[1] Any given Fe^{3+} spin can produce an exchange field at the Eu^{3+} ion by direct cation–cation or indirect cation–anion–cation exchange, the Fe–O–Eu bond angles ranging from 74.1 to 115.0°. In pure $EuFeO_3$ there are four pairs of equivalent Fe^{3+} spins which mutually cancel because of the antiferromagnetic alignment. Substitution of one ion in an equivalent pair by Cr^{3+} will produce an imbalance in the exchange interaction. As a first approximation all four pairs of Fe^{3+} spins are assumed to be equivalent. If the flux density of the molecular exchange field at the Eu^{3+} site due to an iron spin is B_1 and due to a chromium spin is B_2, the total exchange field B_m will be a multiple of $B_0^m = |B_1 - B_2|$, *i.e.* $B_m = nB_0^m$ with $n = 0$—4. The binomial probability for each value of n was calculated and illustrated in Figure 6 of Part 1 of this series.[1] For $x = 0.2$ it was found that 35% of the sites experience a negligible exchange field, and 46% have an exchange field of $B_0^m = |B_1 - B_2|$. The distribution is symmetrical with respect to replacement of x by $1 - x$. This is also a characteristic of the ^{151}Eu linewidth at 85 K (see Figure 2) where the observed magnetic flux density is at least 90% of its saturation value for all samples. In reality B_0^m will have a small spread of values because of non-equivalence of sites, but it is not possible to confirm this.

The ^{151}Eu spectra were computer analysed using the model with five hyperfine fields appropriately weighted. The quadrupole parameters were fixed at the values given above, and the orientation of the electric field gradient tensor and the spin axis (along a) were also fixed.[1,2] In this way an experimental value for B_0^m could be determined. This flux density was then used to calculate the exchange constant of the molecular exchange field, $(\beta/k)B_0^m$, in thermal energy units (K), where β is the Bohr magneton and k is Boltzmann's constant. Thus the values of $(\beta/k)B_0^m$ at 85 K for $x = 0.1$, 0.2, 0.3, 0.4, and 0.5 were 1.74, 1.43, 1.50, 1.30, and 1.18 K. These values of B_0^m will be proportional to the magnetisation of the Fe^{3+} ions, and hence to the average magnetic flux density B_{av} at ^{57}Fe with one or more chromium neighbours (Fe atoms with no chromium neighbours cannot contribute to B_0^m). Following the procedure used for the cobalt phase, these values were extrapolated to the $T = 0$ K limit for Fe^{3+} with one Cr^{3+} neighbour to give a zero-temperature value for the exchange constant of $(\beta/k)B_0^m(0) = 1.7 \pm 0.2$ K.

This value of $(\beta/k)B_0^m(0)$ in $EuFe_{1-x}Cr_xO_3$ can be compared to that of 3.2 ± 0.1 K in $EuFe_{1-x}Co_xO_3$, which it will be remembered contains diamagnetic Co^{3+} ions. The difference is clearly significant, and even though the values are averaged 'effective' parameters it is clear that the exchange field at Eu^{3+} due to a Cr^{3+} ion *has the same sign* as that due to an Fe^{3+} ion when the Eu–O–M bond angle is *ca.* 90°. Since the Co^{3+} ion is non-magnetic, the exchange constant due to Cr^{3+} is $(\beta/k)B_0^m(0) = 1.5 \pm 0.3$ K. The significance of this result with respect to the Fe–O–Cr interaction will be discussed in Part 4 of this series.

Conclusions

A careful study of the phases $EuFe_{1-x}Co_xO_3$ and $EuFe_{1-x}Cr_xO_3$ has shown that the s.t.h.f. in the ^{57}Fe spectrum and the molecular exchange field at the Eu^{3+} ion are sensitive to the nature of the substituent atom. An adequate determination of these quantities is possible for other $EuFe_{1-x}M_xO_3$ phases from measurements at a single composition with $x = 0.2$ to achieve optimum resolution. Such measurements are being carried out for M = Al, Ga, Sc, Mn, and Ni and will be reported elsewhere. Other measurements in progress include the observation of the s.t.h.f. at ^{119}Sn impurity atoms in these solid solutions.

Acknowledgements

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References

1 Part 1, T. C. Gibb, *J. Chem. Soc., Dalton Trans.*, 1983, 873.
2 T. C. Gibb, *J. Chem. Soc., Dalton Trans.*, 1981, 2245.
3 M. Marezio, J. P. Remeika, and P. D. Dernier, *Acta Crystallogr. Sect. B*, 1970, **26**, 2008.
4 Y. Nishihara, *J. Phys. Soc. Jpn.*, 1975, **38**, 710.
5 T. Hashimoto, *J. Phys. Soc. Jpn.*, 1963, **18**, 1140.

6 J. K. Srivastava and R. P. Sharma, *J. Phys. (Paris), Colloq.*, 1974, **C6**, 663.
7 J. M. D. Coey and G. A. Sawatzky, *Phys. Status Solidi B*, 1971, **44**, 673.
8 M. A. Butler, M. Eibschutz, and L. G. Van Uitert, *Solid State Commun.*, 1973, **12**, 499.

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