Magnetic Exchange Interactions in Perovskite Solid Solutions. Part 4.* The Fe^{3+}–O–Cr^{3+} Superexchange Interaction

Terence C. Gibb
Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

A major investigation of magnetic exchange and supertransferred hyperfine field effects in perovskite solid solutions has been carried out using ^{57}Fe, ^{119}Sn, and ^{151}Eu Mössbauer resonances. The primary result has been to establish that the Fe^{3+}–O–Cr^{3+} superexchange coupling in orthoferrite and orthochromite solid solutions is antiferromagnetic, and earlier contradictions have been resolved. Ferromagnetic coupling can only occur in oxides where the bond angle is close to 180°. Exchange interactions involving Mn^{3+} and Ni^{3+} have also been observed in the ^{119}Sn and ^{151}Eu resonances.

It was suggested by Kanamori[1] in 1959 that the 180° superexchange interaction between $Fe^{3+}(d^5)$ and $Cr^{3+}(d^3)$ should be ferromagnetic. If this were true, it should be possible to prepare compounds with an ordered array of these two cations which are insulating ferromagnets with large Curie temperatures, but no success has been reported. The basic concept of the ferromagnetic superexchange was first tested in 1973 by Butler *et al.*[2] when they compared supertransferred hyperfine field (s.t.h.f.) effects in the ^{57}Fe Mössbauer spectra of the antiferromagnetic perovskites $YFeO_3$ and $YCrO_3$ (doped with ^{57}Fe); they claimed that the Fe^{3+}–O–Cr^{3+} superexchange was antiferromagnetic for a bond angle of *ca.* 150°. However, an independent ^{119}Sn Mössbauer study by Ovanesyan and Trukhtanov[3] of the solid solution $LaFe_{1-x}Cr_xO_3$ doped with $CaSnO_3$ resulted in a claim for a ferromagnetic interaction.

These contradictory experiments were strongly criticised by Nishihara[4] on the grounds that the s.t.h.f. contributions from Fe^{3+} and Cr^{3+} were not separately identified. A more detailed ^{57}Fe Mössbauer study of $TbFe_{1-x}Cr_xO_3$ was carried out[4] to measure the s.t.h.f. and zero-point spin reduction effects, and it was claimed that the Fe^{3+}–O–Cr^{3+} superexchange is indeed ferromagnetic. The bond angle θ is slightly dependent on the rare-earth cation, A, and detailed measurements of the magnetic hyperfine field at ^{57}Fe impurity atoms in a series of rare-earth orthochromites, $ACrO_3$, by Moskvin *et al.*[5,6] have been carried out to show that the Fe^{3+}–O–Cr^{3+} superexchange is antiferromagnetic for $142 < \theta < 156°$.

It was against this confusing background that the present series of experiments was initiated; the objectives being to study magnetic hyperfine interactions at ^{57}Fe, ^{119}Sn, and ^{151}Eu nuclei in solid solutions of rare-earth orthoferrite and orthochromite perovskites, with a view to resolving the many contradictions and inconsistencies in the earlier investigations, and to determine the sign of the Fe^{3+}–O–Cr^{3+} superexchange in these perovskites.

In a preliminary paper,[7] the ^{151}Eu resonance in some orthorhombic perovskites was investigated, and the symmetry properties of the electric-field gradient tensor at the Eu site in $EuFeO_3$ and $EuCrO_3$ described in detail. In Part 1 of this series,[8] both ^{57}Fe and ^{151}Eu measurements on the solid solution $EuFe_{1-x}Co_xO_3$ $(0 < x < 1)$ which contains diamagnetic Co^{3+} were described, the s.t.h.f. at ^{57}Fe from neighbouring Fe^{3+} ions was determined, and small magnetic exchange effects were observed at the Eu^{3+} ions and analysed in detail. In Part 2, similar measurements[9] on the solid solution $EuFe_{1-x}Cr_xO_3$ $(0 < x < 1)$ enabled the s.t.h.f. and exchange effects due to Cr^{3+} ions to be measured. In Part 3, a detailed study of various orthoferrite perovskites with La, Eu, or Lu as the rare-earth and with 10% substitution of Al, Ga, Sc, Cr, Mn, Co, or Ni was carried out[10] by observing the s.t.h.f. effects at ^{119}Sn impurity atoms. This systematic series of measurements resolved many outstanding inconsistencies in earlier published work.

In this paper, additional ^{57}Fe and ^{151}Eu data are presented for solid solutions $EuFe_{1-x}M_xO_3$ $(0 < x < 1)$, where M = Al, Ga, Sc, Mn, or Ni, and a detailed and critical discussion of the superexchange interactions is developed in the light of the new data obtained during the present studies.

Experimental

Samples of the solid solutions $EuFe_{0.8}M_{0.2}O_3$ (M = Al, Ga, Sc, Mn, or Ni) were prepared from accurately weighed samples of high purity oxides, ground together in a ball-mill, and fired in air to *ca.* 1 300 °C for a total time of 12—16 d with at least two intermediate grindings. 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 present.

The ^{57}Fe and ^{151}Eu spectra were obtained at various temperatures as previously described[8] using an absorber thickness of 20 mg cm^{-2} of the perovskite to ensure compatability with the earlier results for the cobalt and chromium solid solutions.[8,9]

Results and Discussion

The Hyperfine Field at ^{57}Fe.—The flux density of the magnetic hyperfine field at ^{57}Fe in an antiferromagnetically ordered lattice is determined by a number of different factors. Some of these are temperature dependent effects which are reasonably well understood in terms of molecular field theory and are not important in the present context. Here we are concerned with the saturation flux density (*i.e.* the limiting value as the temperature tends towards 0 K). In the samples used in the present work with effective Curie temperatures greater than 500 K this condition is effectively fulfilled below 100 K.

In the specific case of the Fe^{3+} cation in an isostructural series of orthorhombic rare-earth iron perovskite solid solutions, $AFe_{1-x}M_xO_3$, the largest contribution to the flux density derives from the intrinsic $S = \frac{5}{2}$ spin of the ion, which produces a large negative hyperfine field by core polarisation. When the A and M cations are all tripositive and differ only slightly in size, it may be safely assumed that this term is a constant. The $^6A_1$ configuration of Fe^{3+} is an *S* state, so that any orbital and dipolar contributions to the hyperfine field will be very small in near octahedral co-ordination and also effectively constant.

---

* Part 3 is ref. 10.

The second major contribution is from the supertransferred hyperfine field (s.t.h.f.) which is produced by the spins at neighbouring cation sites by transfer and overlap effects, usually through the intervening anion.[11] This will be almost exclusively due to the first nearest-neighbour cations, and can be expected to be zero if such a cation is diamagnetic. For a near-neighbour cation with a half-filled or more than half-filled *d* shell (*e.g.* Fe^{3+} and Ni^{3+}) the s.t.h.f. produced at ^{57}Fe through a 180° Fe–O–M antiferromagnetic exchange linkage is expected to be negative so that the observed flux density of the hyperfine field *increases*.[2] For a near neighbour with a less than half-filled *d* shell (*e.g.* Cr^{3+} and Mn^{3+}) the s.t.h.f. is positive so that the observed flux density *decreases*. If the 180° Fe–O–M exchange is ferromagnetic then the reverse applies. Thus in principle the sign of the s.t.h.f. can be related to the spin configuration.

A third contribution which seriously affects some experiments is the effect of zero-point spin deviation in antiferromagnets.[11] This is in effect a zero-point motion of the spins; the result of which is that there will be a significant difference between the flux density observed at ^{57}Fe in $AFeO_3$ (magnetically concentrated in Fe), and in for example $ACrO_3$ (magnetically dilute in Fe), which is in addition to any s.t.h.f. effects.

Butler *et al.*[2] attempted to evaluate the s.t.h.f. and zero-point spin deviation effects in $YFeO_3$ and ^{57}Fe-doped $YCrO_3$ which showed experimental flux densities (extrapolated to 0 K) of 54.9 ± 0.2 and 51.65 ± 0.15 T respectively. Although they concluded that the Fe–O–Cr superexchange is antiferromagnetic, this result was fairly criticised by Nishihara[4] on the grounds that they did not experimentally separate the contribution of the nearest-neighbour Cr^{3+} ions to the observed s.t.h.f.

The magnetisation of an Fe^{3+} impurity in $YCrO_3$ falls more rapidly with rising temperature than does the bulk magnetisation of the host lattice.[2] This is because the exchange coupling for Fe–Cr is relatively weak, and it was deduced that $|J(\text{Fe–Cr})/J(\text{Cr–Cr})| \sim 2/3$. However, it was emphasised that although the molecular field theory gives an adequate description of the impurity magnetisation, it yields no information about the sign of the interaction as the equations are independent of the sign to first order.[2]

Nishihara[4] successfully measured s.t.h.f. effects in the solid solutions $TbFe_{1-x}M_xO_3$ (M = Cr or Al). For Cr^{3+} substitution, the observed flux density at 0 K was $55.1 - n(0.91 \pm 0.05)$ T where *n* is the number of Cr^{3+} nearest neighbours, and for Al^{3+} it was $55.2 - n(0.86 \pm 0.05)$ T. Nishihara concluded that the s.t.h.f. at ^{57}Fe due to Cr^{3+} was below measurable limits so that the sign of *J*(Fe–Cr) was not indicated. However, consideration of the flux density for ^{57}Fe-doped $TbCrO_3$ of 51.6 ± 0.2 T in terms of the zero-point spin deviation was held to indicate ferromagnetic coupling; this conclusion has since been contested,[6] and the argument used may well be invalid.

In Parts 1 and 2 it was found[8,9] that there was a significant difference in s.t.h.f. in $EuFe_{1-x}Co_xO_3$ and $EuFe_{1-x}Cr_xO_3$, and that the 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+}.

To corroborate this result, s.t.h.f. effects were measured in an analogous manner for 20% substitution by Al, Ga, Sc, Mn, or Ni, and the results are gathered in the Table. The values tabulated are the flux density, *B*, for 6 Fe^{3+} near neighbours, the incremental decrease, ΔB, when one of these is substituted, and the ionic radius of M using the values of Shannon and Prewitt.[12] It is not certain as to whether the differences in the values for *B* are really significant as they were obtained over a considerable period of time and undoubtedly contain some systematic errors. However, the values for ΔB are considered accurate to within ±0.05 T. In particular the values for Cr^{3+} and Co^{3+} were found to be reproducible within that limit. The value of ΔB for Cr^{3+} is the smallest, and being significantly lower than for diamagnetic Ga, Sc, and Co gives clear evidence that the original deduction regarding the sign of the Cr^{3+} s.t.h.f. is correct.[9] The value for Al^{3+} is anomalous when compared with the other diamagnetic cations, although in good agreement with Nishihara's measurements on the corresponding terbium phases.[4] This is evidently not just a size effect as the ionic radii of Al^{3+} and Co^{3+} are similar, but may be indicative of a different spin-transfer mechanism for Al^{3+}.

Table. Observed flux densities for ^{57}Fe and ^{151}Eu in the solid solutions $EuFe_{0.8}M_{0.2}O_3$

M^{3+}	Ionic radius/pm	*B*/T	ΔB/T	$(\beta/k)B_0^m$/K
Al	53	55.32	0.86	3.2
Ga	62	54.83	1.11	3.0
Sc	73	54.93	1.05	2.5
Cr ($S = \frac{3}{2}$)	61.5	54.64	0.83	1.7
Mn ($S = 2$)	65	55.09 *	1.08 *	1.8
Co ($S = 0$)	52.5	54.75	1.03	3.2
Ni ($S = \frac{1}{2}$)	56	54.98	0.96	2.6

* Measured at 120 K, all other values at 85 K.

Paramagnetic Mn^{3+} ($S = 2$, $t_{2g}^3e_g^1$) and Ni^{3+} ($S = \frac{1}{2}$, $t_{2g}^6e_g^1$) are of interest as they are potentially Jahn–Teller ions. Indeed there were signs of a change in the quadrupole interaction parameter, ε, at 85 K when one or more near neighbours are Mn. This was seen as a small asymmetry in the outermost multiplets of the hyperfine pattern which was absent for the other cations. This effect was much reduced at 120 K, and accordingly the data in the Table are quoted for this temperature. It is possible that the presence of Mn^{3+} induces a static distortion of the lattice at low temperatures. No such effect was detectable for Ni. It is clear that any s.t.h.f. for these ions is very small, although in the case of Ni^{3+} the results favour a s.t.h.f. of the same sign as for Fe^{3+} and Cr^{3+}.

The Hyperfine Field at ^{151}Eu.—Although the ground state of $^{151}Eu^{3+}(f^6, J = 0)$ is nominally diamagnetic, magnetic exchange with neighbouring spins can produce an induced flux density at the europium. This is insignificant in $AFeO_3$ because of the antiferromagnetic coupling, but can be observed for asymmetric near-neighbour configurations in the solid solution. The strength of the exchange can be expressed in terms of the exchange constant in degrees K, $(\beta/k)B_0^m$, for an MM′ pair of nearest-neighbour cations (β is the Bohr magneton, *k* is Boltzmann's constant, and B_0^m is the flux density of the exchange field at the Eu site). The detailed procedure for observing and estimating the exchange constant has been given.[8,9] Symmetrical Fe–Fe or Cr–Cr pairs are antiferromagnetically coupled so that $(\beta/k)B_0^m = 0$. The values (extrapolated to 0 K) for the various solid solutions are given in the Table, and are considered accurate to within ±0.2 K. These values of $(\beta/k)B_0^m$ are plotted as a function of the ionic radius in the Figure. The gradual decrease with increasing ionic radius along the series Co, Al, Ga, Sc is logically consistent with a slight weakening of the exchange by lattice expansion. This correlation plot also demonstrates that the value for $(\beta/k)B_0^m$ is significantly reduced when M = Mn, Cr, or Ni, showing that in all three cases there is a magnetic exchange interaction which has the same sign as that due to Fe^{3+}. It is believed that this is the first occasion on which magnetic exchange effects of Eu^{3+} with Mn^{3+}, Cr^{3+}, and Ni^{3+} have been reported.

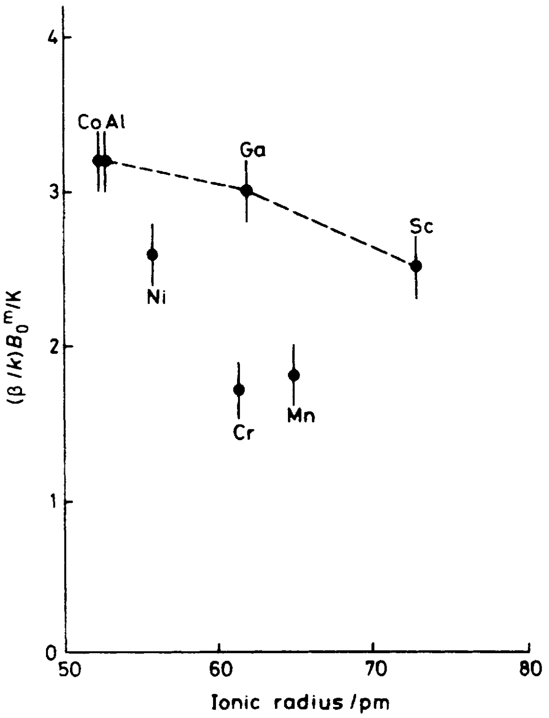

Figure. The exchange constant, $(\beta/k)B_0{}^m$, as a function of the ionic radius of different cations. The dashed line is cosmetic to show how $(\beta/k)B_0{}^m$ decreases with the increasing radius of a diamagnetic cation asymmetrically paired with Fe^{3+}

The Hyperfine Field at ^{119}Sn.—The s.t.h.f. effects at ^{119}Sn doped into $AFe_{1-x}M_xO_3$ perovskites were discussed in detail in Part 3 of this series.[10] The primary result of that work was that the s.t.h.f. at ^{119}Sn produced by Cr^{3+}, Mn^{3+}, or Ni^{3+} substituents has the same sign as that produced by the Fe^{3+} cations of the host lattice.

The Sign of the Fe–O–Cr *Exchange Interaction.*—The reliable determination of the s.t.h.f. effects at ^{57}Fe, ^{119}Sn, and ^{151}Eu by both Fe and Cr nearest-neighbour cations provides fundamental information in a discussion of the Fe–O–Cr exchange interaction in these perovskites. In the first instance it is appropriate to consider the available experimental evidence concerning the homonuclear exchange. In the discussion which follows attention is concentrated on the experimental evidence for the signs and angular dependence of the various interactions, and the reader is referred to the original sources for full details of theoretical calculations.

It is well known that the magnetic exchange mechanism expressed by the Hamiltonian $\mathscr{H} = -2JS_i\cdot S_j$ depends on both the nature of the intervening anion and on the bond angle, and that there may be both a direct cation–cation exchange and an indirect superexchange *via* the anion contributing to J. It is customary to refer to the superexchange interaction in terms of the contributions $J_{90}{}^s$ and $J_{180}{}^s$ for an M–X–M angle of 90° and 180° respectively. At a bond angle φ the interaction constant will be approximately given by equation (1) and

$$J_\varphi{}^s = J_{90}{}^s\sin^2\varphi + J_{180}{}^s\cos^2\varphi \qquad (1)$$

experimental data for various Fe^{3+} and Cr^{3+} oxides have been analysed on this basis.[13] In Fe^{3+} oxides the values deduced were $J_{90}{}^s/k$ *ca.* −3 K, and $J_{180}{}^s/k$ *ca.* −26 K, *i.e.* the interaction is always antiferromagnetic but is substantially stronger for large values of φ. The direct exchange effect J^d appears to be small for Fe^{3+}. In the case of Cr^{3+}, $J_{180}{}^s/k$ *ca.* −28 K (antiferromagnetic) and $J_{90}{}^s/k$ *ca.* +25 K (ferromagnetic) indicate a change of sign at φ *ca.* 135°, but ferromagnetism is not seen when φ is nearly 90° because of a large negative contribution J^d from direct cation–cation overlap.

The average Fe–O–Fe bond angles in the orthoferrites $AFeO_3$ from accurate *X*-ray data[14,15] show a monotonic decrease from La to Lu as the size of the A cation decreases, typical values being 157° for $LaFeO_3$, 148° for $EuFeO_3$, and 144.5° for $LuFeO_3$. The corresponding Néel temperatures (T_N) are 740, 662, and 623 K, and the flux densities of the ^{57}Fe hyperfine field at 0 K are 56.4, 55.2, and 54.55 T, respectively.[16] The decrease in Néel temperature is a direct reflection of the decrease in J(Fe–Fe) as the bond angle decreases (Note:— to avoid confusion the terms ' increase ' and ' decrease ' are used to refer to the magnitude of the modulus of a parameter irrespective of its sign). The bond angles in the corresponding orthochromites $ACrO_3$ are not known, but are not expected to differ substantially from the values in the very similar orthoferrites. The respective Néel temperatures for La, Eu, and Lu are 282, 181, and 112 K, reflecting the large decrease in J(Cr–Cr) as φ tends towards 135°.

A useful result has been obtained[11] from ENDOR studies of ^{27}Al in $LaAlO_3$ doped with Fe and Cr. The Al–O–Al bond angle is unknown, but the compound is reasonably close to cubic symmetry and a value of *ca.* 170° has been estimated. In this instance the s.t.h.f. effects from Fe and Cr are of *opposite* sign. This is in agreement with the theoretical prediction[2] that, for φ = 180° and antiferromagnetic alignment, the s.t.h.f. increases the hyperfine field at ^{57}Fe for Fe^{3+} and decreases the hyperfine field for Cr^{3+}.

The flux density of the hyperfine field at ^{53}Cr as determined from n.m.r. measurements[17] on orthochromites increases slightly from La to Lu. It has been claimed that the variations in the hyperfine field in both the orthoferrites and orthochromites are due solely to changes in the s.t.h.f. with bond angle, and that these have opposite signs. However, the ^{53}Cr n.m.r. data for the orthochromites are only weakly sensitive to angle; covalency and orbital contributions to the observed flux density have been assumed to be negligible, the various factors have not been separated, and in particular the sign of the s.t.h.f. from Cr^{3+} has not in fact been determined.

The angular dependence of J_φ(Fe–Cr) has been measured by observing the ^{57}Fe resonance in doped orthochromites.[5] A plot of the reduced flux density $B(T)/B(0)$ as a function of reduced temperature T/T_N is markedly sensitive to A, and can be interpreted directly using molecular field theory to give a value for $|J_\varphi(\text{Fe–Cr})|$, but *not* its sign. $|J_\varphi(\text{Fe–Cr})|/k$ increases from 3.6 K for ^{57}Fe-doped $LaCrO_3$ to 6.8 K for ^{57}Fe-doped $LuCrO_3$ as the bond angle decreases from *ca.* 157° to *ca.* 144°. The flux density of the hyperfine field $|B(0)|$ actually increases from La to Lu by *ca.* 0.9 T as the s.t.h.f. from 6 Cr^{3+} nearest neighbours changes with decreasing bond angle, *i.e.* in the opposite sense to the change in s.t.h.f. from Fe^{3+} nearest neighbours.[5] Extrapolation suggests that J_φ(Fe–Cr) probably changes sign at φ *ca.* 162°, and it has been proposed that J_φ(Fe–Cr) is positive (ferromagnetic) for $162 < \varphi < 180°$ with $J_{180}(\text{Fe–Cr})/k = +4.5$ K, and negative (antiferromagnetic) for $\varphi < 162°$.

The present work has shown clearly that the s.t.h.f. at ^{57}Fe from Cr^{3+} and Fe^{3+} in $EuFe_{0.8}Cr_{0.2}O_3$ have the same sign and increase the flux density $|B(0)|$ (which is in fact negative in sign). Thus within the range $144 < \varphi < 157°$ it seems that the s.t.h.f. due to Fe^{3+} increases and that due to Cr^{3+} decreases as φ increases. This can be shown to be consistent with an antiferromagnetic alignment of Fe^{3+} and Cr^{3+}, *i.e.* J_{148}(Fe–

Cr) is negative.[5] However, it should be noted that in that work the experimental data could have been interpreted in an alternative way with a s.t.h.f. from Cr^{3+} of opposite sign which increased as φ increases. This possibility has now been eliminated.

The observed decrease in the s.t.h.f. at ^{57}Fe from Cr^{3+} with increase in φ suggests that the s.t.h.f. also changes sign at *ca.* 162°, which would be in agreement with the s.t.h.f. results [11] for Fe- and Cr-doped $LaAlO_3$.

The ^{57}Fe results are therefore fully consistent with an *antiferromagnetic* Fe–O–Cr coupling in orthoferrite–orthochromite solid solutions.

The M–O–Eu *Exchange Interaction.*—Any interpretation of the ^{151}Eu data is more speculative because the detailed mechanism of the exchange with Eu^{3+} is unknown. However, the new results show that magnetic exchange interactions for Fe^{3+} and Cr^{3+} have the same sign. Some useful data are available for iron garnet materials. ^{151}Eu Mössbauer measurements have convincingly shown [18] that the molecular exchange field $(\beta/k)B_0^m$ = *ca.* 26 K at the Eu^{3+} ions on c-sites in $Eu_3Fe_5O_{12}$ is produced largely by the 2 Fe^{3+} ions at neighbouring tetrahedrally co-ordinated d-sites for which the Fe–O–Eu bond angle is *ca.* 92°. The 4 Fe^{3+} ions on a-sites (Fe–O–Eu *ca.* 103°) and 4 Fe^{3+} ions on d-sites (Fe–O–Eu *ca.* 122°) contribute no more than 12% of the total exchange. Independent e.s.r. measurements on $Eu_3Ga_5O_{12}$ doped with Fe^{3+} ions on a-sites show [19] that the Eu^{3+}–Fe^{3+} exchange is very weak and ferromagnetic. Similar e.s.r. measurements for Mn^{2+} impurities ($3d^5$, $S = \frac{5}{2}$) in SmS, SmSe, and SmTe ($4f^6$, $J = 0$) have shown [20] that the Mn–Sm interactions are large and antiferromagnetic in SmS (J = 39 K) but decrease rapidly in magnitude as the lattice constant increases along the series. This observation was held to be inconsistent with normal superexchange *via* the chalcogen in the NaCl-type lattices (Mn–S–Sm is 180 or 90°), which by analogy with data for MnO, α-MnS, and α-MnSe should not be so sensitive to the lattice constant. Instead, it was proposed that the dominant exchange is a *direct* cation–cation interaction. For a given anion the 90° direct cation–cation interaction would be much weaker for Fe^{3+} (radius 64.5 pm) and Eu^{3+} (95 or 107 pm in six- or eight-co-ordination respectively), compared to isoelectronic Mn^{2+} (82 pm) and Sm^{2+} (*ca.* 119 pm in six-co-ordination), because of the large decrease in overlap. From a comparison of the available data it appears that the Fe^{3+}–Eu^{3+} exchange in $Eu_3Fe_5O_{12}$ is indeed weaker than the Mn^{2+}–Sm^{2+} exchange in SmS.

If the dominant exchange mechanism in $Eu_3Fe_5O_{12}$ is indeed direct cation–cation exchange, then the large decrease observed on increasing the Fe–O–Eu angle from 92 to 122° is easily understood. Similarly, the low value of $(\beta/k)B_0^m$ = 3 K in $SrEu_2Fe_2O_7$ for a single Fe–Eu exchange and an Fe–O–Eu angle of 154° is consistent [21] with a comparatively weak superexchange *via* oxygen, although direct comparison with $Eu_3Fe_5O_{12}$ is made more difficult by the longer Fe–O bond distance associated with six-co-ordination of Fe in this instance which would also decrease the strength of the exchange.

The magnetisation of $Eu_3Fe_5O_{12}$ is lower than in $Y_3Fe_5O_{12}$ because the Eu^{3+} moments couple antiparallel to the resultant Fe^{3+} moments.[22] The 3 Fe^{3+} ions per formula unit on tetrahedral d-sites couple antiparallel to the 2 Fe^{3+} ions on a-sites, so that the Eu^{3+} moments are therefore antiparallel to the Fe^{3+} ions on d-sites. This observation is fully consistent with the Mn^{2+}–Sm^{2+} interaction in SmS described above. Since the Fe–O–Eu bond angles in $EuFeO_3$ range from 82 to 115°, the Fe^{3+}–Eu^{3+} exchange should be closely analogous to that in $Eu_3Fe_5O_{12}$. Therefore it can be confidently assumed that in the solid solutions an uncompensated Fe^{3+} ion will couple *antiparallel* (antiferromagnetic) to the moment at the Eu^{3+} ion. Since the Fe^{3+}–O–Cr^{3+} superexchange is antiferromagnetic, it can be seen that Cr^{3+}–Eu^{3+} exchange should also be antiferromagnetic. This is fully consistent with the observed decrease in the exchange constant (see Table) when a diamagnetic atom paired with Fe^{3+} is replaced by Cr^{3+}.

Although the s.t.h.f.s at ^{57}Fe produced by Mn^{3+} and Ni^{3+} were too small to observe with confidence, the exchange coupling with Eu^{3+} is clearly observed as a similar reduction in the exchange constant, and is consistent with antiferromagnetic coupling.

The M–O–Sn *Superexchange Interaction.*—The orthoferrites, orthochromites and their solid solutions can be conveniently doped with ^{119}Sn introduced as $CaSnO_3$. The experimental results for the s.t.h.f. at ^{119}Sn in various phases have been presented in Part 3 of this series. Previous measurements on the phase ^{119}Sn–$LaFe_{1-x}Cr_xO_3$ had been interpreted in favour of a ferromagnetic Fe–O–Cr superexchange.[3] Subsequently the result was questioned by Nishihara [4] who considered that the s.t.h.f. produced by Cr^{3+} had not been experimentally separated from the dominant Fe^{3+} contribution. In Part 3 it was shown that in various orthoferrite and orthochromite solid solutions the s.t.h.f. at ^{119}Sn produced by Cr^{3+} (also Mn^{3+} and Ni^{3+}) has the same sign as that produced by the Fe^{3+} cations of the host lattice. This result was in agreement with the earlier claim,[3] but the criticism of Nishihara has been eliminated.

The s.t.h.f. at ^{119}Sn in both orthoferrites and orthochromites has been examined in considerable detail from a theoretical viewpoint.[23,24] For $ACrO_3$ doped with ^{119}Sn, the dependence of the observed flux density on the Sn–O–Cr bond angle φ can be approximated by equation (2), where B_{90} = 23.9 T and

$$B_{\text{obs.}} = B_{90}\sin^2\varphi + B_{180}\cos^2\varphi \qquad (2)$$

B_{180} = −0.8 T. Although extrapolation from the necessarily limited range of φ which can be observed is not beyond criticism, it is significant that a reverse of the sign of $B_{\text{obs.}}$ is predicted at *ca.* 170° (although the choice of sign has not been confirmed experimentally). Direct evidence in support of this possibility comes from the solid solution of ^{119}Sn-doped $Ca_{1-x}Sr_xMnO_3$, where the bond angle varies from *ca.* 157° in $CaMnO_3$ to 180° in cubic $SrMnO_3$, and Mn^{4+} is isoelectronic with Cr^{3+}. The narrowing of the ^{119}Sn resonance observed [25] at x = 0.875 has been interpreted [24] as evidence for a change in sign of $B_{\text{obs.}}$ analogous to that predicted for Cr^{3+}.

For $AFeO_3$ doped with ^{119}Sn, the dependence of the observed flux density on the Sn–O–Fe bond angle can be approximated [24] by equation (3) with α *ca.* 0.8 T, β *ca.* 24.1 T, γ *ca.* 55.1

$$B_{\text{obs.}} = \alpha + \beta\cos\varphi + \gamma\cos^2\varphi \qquad (3)$$

T. The sign of $B_{\text{obs.}}$ is independent of φ. Evidence for the sign of $B_{\text{obs.}}$ comes from data [26] for $Y_3Fe_5O_{12}$ doped with ^{119}Sn. Tin substitutes at the octahedral a-site, but the s.t.h.f. is produced by the Fe^{3+} cations at the tetrahedral d-site. The superexchange bond angle is 127°. In an applied magnetic field the ^{119}Sn flux density increases, showing that $B_{\text{obs.}}$ is parallel to it. The spins on the three d-sites couple parallel to the external field but antiparallel to the a-sites. Thus for φ = 127° the s.t.h.f. at the tin is parallel to the spin of the Fe^{3+} cation (positive in sign). This should also be the case in the orthoferrites. The theoretical analysis of the exchange mechanisms and orbital overlap for both the orthochromite and orthoferrites predicts that the sign of $B_{\text{obs.}}$ should be the same in both cases.[24] Thus in the solid solutions the observation [10] that the s.t.h.f. from Fe^{3+} has the same sign as that from Cr^{3+} is only consistent if they have parallel spins, *i.e.* if the Fe^{3+}–O–Cr^{3+} superexchange is *antiferromagnetic*.

The Mn *and* Ni *Interactions*.—Although in the case of Mn^{3+} and Ni^{3+} clear evidence has been found for exchange with Eu^{3+} and for a s.t.h.f. at ^{119}Sn, no attempt has been made to analyse these in detail. This is largely because of the electron configurations of Mn^{3+} ($S = 2$, $t_{2g}^3e_g^1$) and Ni^{3+} ($S = \frac{1}{2}$, $t_{2g}^6e_g^1$) in octahedral co-ordination to oxygen: both have the potential to give Jahn–Teller distortions. Some evidence for the latter was found in the ^{57}Fe data for Mn^{3+}, but a major investigation of the whole solid solution is required. While Fe^{3+} ($t_{2g}^3e_g^2$) and Cr^{3+} (t_{2g}^3) in ideal octahedral co-ordination show superexchange interactions which only depend upon the cation–anion–cation bond angle φ, the superexchange interaction of Fe^{3+} with Mn^{3+} (or Ni^{3+}) would depend on two angles θ and φ to specify the crystal-field axis of the latter.[5] It seems unlikely that such a complication could be analysed successfully from s.t.h.f. measurements of the kind reported here.

Conclusions

The experimental data for the ^{57}Fe, ^{119}Sn, and ^{151}Eu resonances in solid solutions of rare-earth orthochromites and orthoferrites have been found to be completely consistent with an antiferromagnetic Fe^{3+}–O–Cr^{3+} superexchange. Ferromagnetic superexchange may occur if the bond angle is close to 180°, but this cannot be achieved in these particular solid solutions.

Acknowledgements

Acknowledgement is made to the S.E.R.C. for financial support.

References

1 J. Kanamori, *J. Phys. Chem. Solids*, 1959, **10**, 87.
2 M. A. Butler, M. Eibschutz, and L. G. Van Uitert, *Solid State Commun.*, 1973, **12**, 499.
3 N. S. Ovanesyan and V. A. Trukhtanov, *JETP Lett.*, 1973, **17**, 67.
4 Y. Nishihara, *J. Phys. Soc. Jpn.*, 1975, **38**, 710.
5 A. S. Moskvin, N. S. Ovanesyan, and V. A. Trukhtanov, *Hyperfine Interact.*, 1975, **1**, 265.
6 A. S. Moskvin and I. G. Bostrem, *Sov. Phys. Solid State*, 1977, **19**, 1532.
7 T. C. Gibb, *J. Chem. Soc., Dalton Trans.*, 1981, 2245.
8 T. C. Gibb, *J. Chem. Soc., Dalton Trans.*, 1983, 873.
9 T. C. Gibb, *J. Chem. Soc., Dalton Trans.*, 1983, 2031.
10 T. C. Gibb, *J. Chem. Soc., Dalton Trans.*, 1983, 2035.
11 J. Owen and D. R. Taylor, *J. Appl. Phys.*, 1968, **39**, 791.
12 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 1969, **25**, 925.
13 K. Motide and S. Miyahara, *J. Phys. Soc. Jpn.*, 1970, **28**, 1188.
14 M. Marezio, J. P. Remeika, and P. D. Dernier, *Acta Crystallogr., Sect. B*, 1970, **26**, 2008.
15 M. Marezio and P. D. Dernier, *Mat. Res. Bull.*, 1971, **6**, 23.
16 M. Eibschutz, S. Shtrikman, and D. Treves, *Phys. Rev.*, 1967, **156**, 562.
17 M. A. Butler, M. Eibschutz, and L. G. van Uitert, *Phys. Rev. B*, 1972, **6**, 51.
18 I. Nowik and S. Ofer, *Phys. Rev.*, 1967, **153**, 409.
19 M. T. Hutchings, C. G. Windsor, and W. P. Wolf, *Phys. Rev.*, 1966, **148**, 444.
20 R. J. Birgeneau, E. Bucher, L. W. Rupp, and W. M. Walsh, *Phys. Rev. B*, 1972, **5**, 3412.
21 T. C. Gibb, *J. Phys. C*, 1981, **14**, 1985.
22 W. P. Wolf and J. H. Van Vleck, *Phys. Rev.*, 1960, **118**, 1490.
23 A. S. Moskvin, N. S. Ovanesyan, and V. A. Trukhtanov, *Hyperfine Interact.*, 1977, **3**, 429.
24 A. S. Moskvin, N. S. Ovanesyan, and V. A. Trukhtanov, *Hyperfine Interact.*, 1977, **5**, 13.
25 M. Takano, Y. Takeda, M. Shimada, T. Matsuzawa, T. Shinjo, and T. Takada, *J. Phys. Soc. Jpn.*, 1975, **39**, 656.
26 V. I. Goldanskii, M. N. Levisheva, E. F. Makarov, G. V. Novikov, and V. A. Trukhtanov, *JETP Lett.*, 1966, **4**, 42.

Received 15*th June* 1983; *Paper* 3/1017