Magnetic Exchange Interactions in Perovskite Solid Solutions. Part 3.[1] Tin-119 Mössbauer Spectra of Doped Iron Perovskite Solid Solutions

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A detailed study has been made of supertransferred hyperfine field (s.t.h.f.) effects at ^{119}Sn doped into various perovskites with the formula $(A_{0.95}Ca_{0.05})(Fe_{0.85}M_{0.10}Sn_{0.05})O_3$ with A = La, Eu, or Lu and M = Al, Ga, Sc, Cr, Mn, Co, or Ni. The observed s.t.h.f. for ^{119}Sn with six nearest-neighbour Fe^{3+} cations is strongly dependent on the nature of A, but is almost independent of the M substituent. The s.t.h.f. is also sensitive to the radius of a diamagnetic M^{3+} substituent at the nearest-neighbour sites. The paramagnetic substituents Cr^{3+}, Mn^{3+}, and Ni^{3+} have been shown to give a s.t.h.f. at ^{119}Sn which has the same sign as that produced by the Fe^{3+} cations of the host lattice.

Detailed studies [1,2] of the solid solutions $EuFe_{1-x}Co_xO_3$ and $EuFe_{1-x}Cr_xO_3$ $(0 < x < 1)$ by ^{57}Fe and ^{151}Eu Mössbauer spectroscopy have given interesting new evidence concerning the magnetic exchange interactions involving Eu^{3+}, Fe^{3+}, and the substituent metal cation. The ^{57}Fe Mössbauer spectrum for $EuFeO_3$ is a conventional six-line magnetic hyperfine pattern at temperatures below the Curie temperature. When $x > 0$ the spectra show additional hyperfine components which can be attributed to Fe^{3+} ions with one or more substituent ions on the six nearest-neighbour Fe^{3+} sites. Detailed analysis has shown that it is possible to compare the supertransferred hyperfine field (s.t.h.f.) at ^{57}Fe due to different substituents, and it was found that the s.t.h.f. due to a Cr^{3+} nearest-neighbour cation has the same sign as that due to a Fe^{3+} cation on the same site.

The ^{151}Eu resonance in the solid solutions shows magnetic broadening, and the molecular exchange field at Eu^{3+} due to a Cr^{3+} ion has the same sign as that due to a Fe^{3+} ion.[1] These results are highly relevant to a discussion of the Fe–O–Cr superexchange in $EuFe_{1-x}Cr_xO_3$. This superexchange has been claimed to be both antiferromagnetic and ferromagnetic by various authors. The significance of these results, together with similar data for other substituent metals, will be discussed more fully in Part 4 of this series.

This paper presents a detailed study of s.t.h.f. effects at ^{119}Sn doped into various perovskites to give the phases $(A_{0.95}Ca_{0.05})(Fe_{0.85}M_{0.10}Sn_{0.05})O_3$ with A = La, Eu, or Lu, and M = Al, Ga, Sc, Cr, Mn, Co, or Ni. This study was carried out to provide additional information regarding the Fe–O–Cr superexchange, and to investigate several anomalies apparent in earlier investigations.

Experimental

Solid solutions of a rare-earth-metal orthoferrite $AFeO_3$ (A = La, Eu, or Lu) containing 10 mole % of AMO_3 (M = Al, Ga, Sc, Cr, Mn, Co, or Ni) and 5 mole % of $CaSnO_3$ were prepared by accurately weighing samples of high-purity oxides or carbonates in the appropriate proportions, grinding together in a ball-mill, and firing in air to *ca.* 1 400 °C for *ca.* 15 d with two intermediate grindings. The products were characterised by *X*-ray diffraction using a Philips diffractometer and nickel-filtered Cu-K_α radiation. All samples gave patterns characteristic of the orthorhombic perovskite with no other phases present. The ^{119}Sn Mössbauer spectra were recorded at 85 K using established techniques and a source matrix of $Ca^{119m}SnO_3$. The data were analysed by digital computer using a theoretical model described in the text.

Results and Discussion

Considerable data are now available which show that when diamagnetic Sn^{4+} cations are substituted into a magnetic host lattice the ^{119}Sn Mössbauer resonance displays a large magnetic hyperfine splitting due to a supertransferred hyperfine field (s.t.h.f.). This field results from an induced spin density in the *s* shells of the tin due to the paramagnetic cation of the host lattice, and is produced by a covalent overlap with the intermediate anion. It is therefore sensitive to the identity of the anion and the paramagnetic cation and to the bond distances and the tin–anion–cation bond angle.

Many of the rare-earth-metal perovskites readily form solid solutions with $CaSnO_3$ in which the Ca^{2+} ions occupy the rare-earth sites and Sn^{4+} ions occupy the M^{3+} cation sites. Although several investigations of ^{119}Sn-doped perovskites have been reported, the results cannot always be compared directly because the rare-earth-metal cation is not necessarily the same. An early paper by Bokov *et al.*[3] showed evidence for s.t.h.f. effects in $YFeO_3$, $LaCrO_3$, and $(LaCa)MnO_3$ all doped with $CaSnO_3$, and found that the s.t.h.f. due to $Cr^{3+}(d^3)$ ions was substantially less than that due to $Fe^{3+}(d^5)$ ions. Solid solutions of $YFeO_3$ and $GdFeO_3$ with 10% $CaSnO_3$ gave s.t.h.f. effects with a flux density at 78 K of 17.6 and 19.5 T respectively.[4] The Curie temperature of these phases is *ca.* 586 K, so that the field at ^{119}Sn at 78 K is close to its saturation value; it is therefore clear that the s.t.h.f. depends strongly on the rare-earth-metal cation. A more detailed study [5] of eleven rare-earth-metal orthoferrites containing $CaSnO_3$ showed a monotonic decrease in the s.t.h.f. from lanthanum to lutetium which was correctly attributed to a corresponding decrease in the Sn–O–Fe bond angle.

Solid solutions of $NdFeO_3$ containing 5—30 mole % of $CaSnO_3$ were found to show complex hyperfine patterns.[6,7] At low tin concentrations, nearly all of the sites occupied by tin have six Fe^{3+} nearest-neighbour cations, but as the tin content increases there is an increase in the number of tin sites with one or more Sn^{4+} near neighbours. The observed flux density at 78 K could be expressed by $(21.6 - 2.9n)$ T where n is the number of near-neighbour Sn^{4+} ions. Similar data for $LaFeO_3$ gave $(26.0 - 3.5n)$ T, and it was concluded that in both cases 81% of the s.t.h.f. derived from the nearest-neighbour cation sites and 19% from more distant neighbours, both contributions having the same sign. The present work does not support this conclusion.

An independent investigation [8] of the phase $LaFe_{1-x}Cr_xO_3$ with 2.5 mole % $CaSnO_3$ showed that both Fe^{3+} and Cr^{3+} produce a s.t.h.f. at the tin. The total flux density could be expressed as $4.2(6 - n) + 0.8n = (25.2 - 3.4n)$ T where n is the number of Cr^{3+} nearest-neighbour cations; thus for $n = 0$ the flux density was 25.2 T and for $n = 6$ it was 4.8 T. Moreover, it did not appear necessary to invoke contributions from more distant neighbours. Brief details were also given of a calculation which was said to support a ferromagnetic Fe^{3+}–O–Cr^{3+} exchange. However, a subsequent paper by Nishihara[9] on $TbFe_{1-x}Cr_xO_3$ referred to the similarity of data for $LaFeO_3$ with Sn^{4+} and Cr^{3+} substitution,[6-8] and maintained that the sign of the Fe^{3+}–O–Cr^{3+} exchange could not be determined from these results.

Data are also available[10] for $LaFeO_3$ doped with 2 mole % of $CaSnO_3$ and 7 mole % of $LaAlO_3$, $LaGaO_3$, or $LaScO_3$; the corresponding values for the flux density of the s.t.h.f. were $(25.2 - 3.3n)$, $(25.2 - 4.1n)$, and $(25.2 - 4.7n)$ T. Although the s.t.h.f. for Sn^{4+} with six Fe^{3+} nearest neighbours was effectively independent of the substituent cation, the s.t.h.f. with one nearest neighbour substituted showed marked variations. The effect was considered to be due to small changes in the Fe^{3+}–O–Sn^{4+} bond angles (less than 1°) as the lattice accommodates substituents of different sizes, and effects from more distant neighbouring cations were thought to be negligible. More recently the Fe^{3+}–O–Sn^{4+} and Cr^{3+}–O–Sn^{4+} interactions have been considered in detail from a theoretical viewpoint with particular emphasis on the effect of the bond angle.[11,12]

These papers have resulted in some confusion as to whether the relative signs of the s.t.h.f. produced at Sn^{4+} by Fe^{3+} and Cr^{3+} neighbours can be determined. Furthermore, the energy-conversion parameters used have not been given so that there is the possibility of systematic error between different laboratories. Therefore some of these measurements have been repeated, as part of a more extensive investigation, with the primary objective of resolving these problems. Data for Sn^{4+} impurity in various rate-earth-metal orthoferrites and orthochromites[12] show that the s.t.h.f. at Sn^{4+} due to six Fe^{3+} nearest-neighbour cations decreases substantially from La to Lu as the Fe–O–Sn bond angle decreases, while the corresponding s.t.h.f. due to six Cr^{3+} cations increases. Thus in a solution of $LaFeO_3$ and $LaCrO_3$, in which the s.t.h.f. due to Fe^{3+} ions is at a maximum, the s.t.h.f. due to Cr^{3+} ions will be small (about 15% of that due to Fe^{3+}). In the case of $LuFeO_3$ and $LuCrO_3$ the s.t.h.f. due to Cr^{3+} ions will be much larger (about 50% of that due to Fe^{3+}). It therefore seemed advantageous to change the rare-earth-metal cation, and for this reason the present investigation has included perovskite solid solutions derived from $LaFeO_3$, $EuFeO_3$, and $LuFeO_3$. The average Fe–O–Fe bonds angles from accurate *X*-ray data[13,14] are 157, 148, and 144.5° respectively, and it is believed that the Cr–O–Cr bond angles are very similar. The average Fe–O bond distances are 200.6, 201.3, and 201.0 pm respectively, and the FeO_6 octahedra are very close to regular. It is therefore reasonable to assume that the large observed differences in the s.t.h.f. at the tin nucleus are mainly due to the variation in the Fe–O–Sn bond angle.

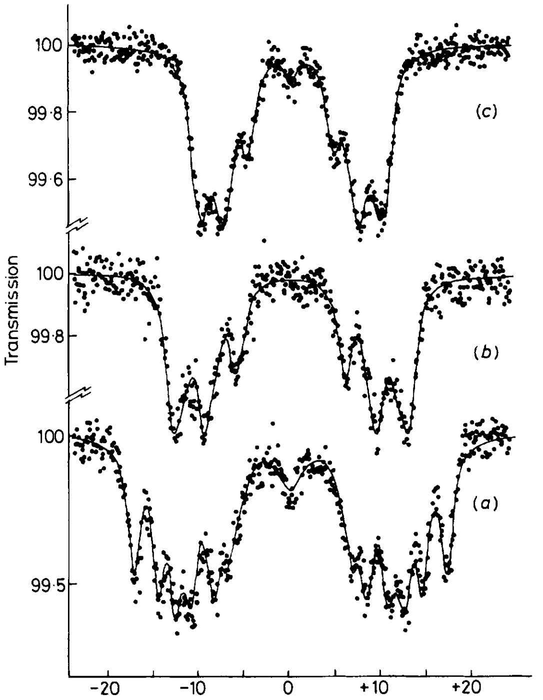

Figure 1. ^{119}Sn Mössbauer spectra at 85 K of solid solutions of (*a*) $(La_{0.95}Ca_{0.05})(Fe_{0.85}Ga_{0.10}Sn_{0.05})O_3$, (*b*) $(Eu_{0.95}Ca_{0.05})(Fe_{0.85}Ni_{0.10}Sn_{0.05})O_3$, and (*c*) $(Lu_{0.95}Ca_{0.05})(Fe_{0.85}Cr_{0.10}Sn_{0.05})O_3$

The solid solutions of $AFeO_3$ (A = La, Eu, or Lu) were prepared containing 10 mole % of AMO_3 and 5 mole % of $CaSnO_3$ with the dual aim of giving a strong ^{119}Sn Mössbauer resonance and an easily observable fine structure. In a random solid solution at these concentrations 38% of Sn atoms have six Fe nearest-neighbour cations, 27% have five Fe and one M cation, and 13% have five Fe and one Sn cation. In total there are eight different new-neighbour environments which contribute more than 1% to the spectrum (but only five more than 2%). All eight of these were included in the computed data analysis by assuming that each cation contributed a flux density characteristic of the cation, so that the total flux density $B_{\rm eff}$ at the Sn nucleus was given by equation (1) where

$$B_{\rm eff} = n_1B({\rm Fe}) + n_2B({\rm M}) + n_3B({\rm Sn}) \qquad (1)$$

$n_1 + n_2 + n_3 = 6$, and each six-line hyperfine pattern contributing to the actual spectrum was weighted according to the binomial probability. In retrospect it would have been possible to reduce the tin content to *ca.* 2 mole % and thereby reduce the importance of *B*(Sn). However, the spectra were clearly dominated by *B*(Fe) and *B*(M), and these parameters were easily determined. In the event the values for *B*(Sn) were obtained separately from solid solutions of $AFeO_3$ with 10 mole % $CaSnO_3$, and were then kept as fixed parameters for the ternary solid solutions. Only one value each was specified for the chemical shift and linewidth, and any quadrupole interactions were assumed negligible.

Typical Mössbauer spectra for the La/Ga, Eu/Ni, and Lu/Cr solid solutions are shown in Figure 1. In some samples the spectra showed a small paramagnetic ^{119}Sn component. This was believed to be a tin-rich phase which was either the result of selective evaporation of Ca, or had precipitated from the perovskite during cooling, and was not detected in the *X*-ray data. Quench-cooling was not possible with the furnace arrangement used, and after investigation it was concluded that the presence of a small paramagnetic component had no noticeable effect on the study of the s.t.h.f. The solid lines in Figure 1 represent the computed curves on the basis of the model outlined above. The values for the flux density of the hyperfine field were obtained using values of 23.871 keV (*ca.* 3.8×10^{-15} J) for the γ-ray energy, $\mu_g = -1.0461$ nuclear magnetons for the ground-state magnetic moment, and $\mu_e/\mu_g = -0.645$ for the ratio of the excited and ground state moments. The latter value is somewhat variable for ^{119}Sn because of a hyperfine anomaly; the chosen value was obtained from the s.t.h.f. in an iron garnet system,[15] which is considered to be analogous to the perovskites.

The values for $B_{\rm eff}$ corresponding to six Fe^{3+} nearest-

Table. Effective magnetic flux densities B_6 and B_5 in Tesla at 85 K

	$LaFeO_3$		$EuFeO_3$		$LuFeO_3$	
M	B_6	B_5	B_6	B_5	B_6	B_5
Sn	25.2	21.5	19.6	17.3	15.8	14.5
Al	25.8	22.2	19.8	18.4	—	—
Ga	25.3	21.2	19.2	16.0	15.3	12.4
Sc	25.1	20.3	?	?	—	—
Cr	25.4	22.1	19.5	18.1	15.5	14.2
Mn	25.8	24.7	19.7	18.7	—	—
Co	25.4	22.1	19.5	18.3	15.6	14.0
Ni	25.5	23.5	19.4	18.5	—	—

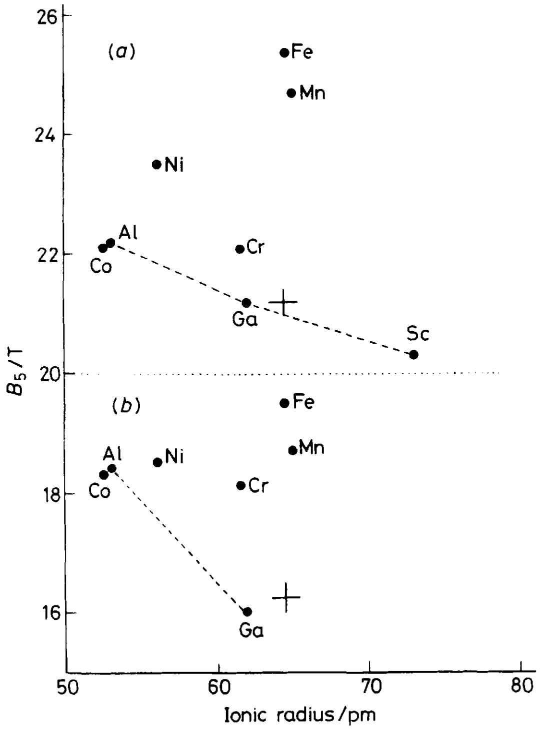

Figure 2. The flux density of the s.t.h.f. for Sn^{4+} with five Fe^{3+} and one M^{3+} nearest neighbour (B_5) as a function of the ionic radius of M^{3+} in (*a*) $LaFeO_3$ and (*b*) $EuFeO_3$. The cross represents a hypothetical diamagnetic cation with the same radius as Fe^{3+}. The values plotted for Fe^{3+} are the average values of B_6. The dashed lines are cosmetic and show the relationship between Al^{3+}, Ga^{3+}, and Sc^{3+}

neighbour cations (B_6) and to five Fe^{3+} plus one M^{3+} cation (B_5) are shown in the Table. Where previously published data are available, the agreement is quite good considering that some measure of systematic error may have resulted from the choice of energy-conversion factors in different laboratories. Only a few samples were made using $LuFeO_3$ because it was felt that the lower resolution was a disadvantage, and that the comparison of $LaFeO_3$ and $EuFeO_3$ gave adequate data. The experimental values for B_{eff} are considered accurate to within ± 0.2 T.

Although it became clear that the representation of B_{eff} as a linear sum might not be strictly applicable to all of the near-neighbour environments, the spectra are dominated by the 78% of sites with $n_1 = 6$ or 5, so that the s.t.h.f. values for these sites can be obtained with only small errors. The minority contributions mainly affect the intensities of the inner region of the spectrum, and because of the low resolution cannot be observed with precision.

Several important features can be noted. The s.t.h.f. at ^{119}Sn with an environment of six Fe^{3+} nearest-neighbour cations is almost independent of the other substituent, but does depend markedly on the rare-earth-metal cation. The experimental values for the $LaFeO_3$ phases range from 25.1 to 25.8 T, and for $EuFeO_3$ from 19.2 to 19.8 T; these values were obtained over a period of time, and there is undoubtedly some contribution from systematic errors. Nevertheless, there is a strong correlation between pairs of values for $LaFeO_3$ and $EuFeO_3$ with the same substituent, and it seems certain that there is some genuine variation in the s.t.h.f. The large differences in s.t.h.f. between tin-doped $LaFeO_3$, $EuFeO_3$, and $LuFeO_3$ are undoubtedly the result of a decrease in the Sn–O–Fe bond angle, although it should be remarked that the substitution of Fe^{3+} by the larger Sn^{4+} ion must result in some degree of local distortion. However, it is reasonable to assume that the general trend in bond angles recorded in the pure phases is preserved in the solid solutions.

The s.t.h.f. at ^{119}Sn with an environment of five Fe^{3+} and one M^{3+} nearest-neighbour cations is strongly dependent on the nature of M^{3+}, but is only slightly influenced by more distant irregularities in the lattice. The values observed can be rationally explained by considering the effective ionic radius and the electronic configuration of the M^{3+} ion. The observed values of B_5 in $LaFeO_3$ and $EuFeO_3$ are plotted in Figure 2 as a function of the M^{3+} radius, using values tabulated by Shannon and Prewitt.[16] The flux density of the s.t.h.f. decreases uniformly with increasing ionic size for the diamagnetic cations Al^{3+}, Ga^{3+}, and Sc^{3+}, in agreement with previous data.[10] Note the close correlation of Co^{3+} (t_{2g}^6, $S = 0$) with Al^{3+}, and also the s.t.h.f. indicated by a cross for a hypothetical diamagnetic cation with the same radius as Fe^{3+}. This suggests that there is little or no contribution to the s.t.h.f. from more distant cations.

It seems likely that insertion of a larger cation causes an increased distortion in the environment of the Sn^{4+} ion so that one or more Sn–O–Fe bond angles decrease slightly, and hence cause the observed reduction in the s.t.h.f. Conversely, insertion of a smaller cation causes a widening of some of the bond angles. Any influence of a nearby charge-compensating Ca^{2+} ion appears to be small.

Although a sample of $EuFeO_3$ with 10 mole % $EuScO_3$ and 5 mole % $CaSnO_3$ was prepared and characterised as an orthorhombic perovskite, the ^{119}Sn Mössbauer spectrum proved to be incompatible with the analysis applied to all the other samples. The spectrum was reproducible, and was not affected by re-annealing the sample. The s.t.h.f. due to six Fe^{3+} neighbours was clearly less than expected, but a satisfactory curve-fit could not be achieved within the framework described above. The cause of this was not established, but it seems possible that the comparatively large $M^{3+} : A^{3+}$ radius ratio in this sample was introducing some additional distortions.

Examination of the results for Cr^{3+} (t_{2g}^3, $S = \frac{3}{2}$) substitution shows clearly that the s.t.h.f. is larger than for a diamagnetic cation of the same size, and proves that the s.t.h.f. contribution due to a Cr^{3+} ion is of the same sign as that due to an Fe^{3+} ion. The implications of this observation will be discussed fully in Part 4. The decrease in s.t.h.f. due to Fe^{3+} and the increase due to Cr^{3+} on changing the host lattice from $LaFeO_3$ to $EuFeO_3$ agree with the prediction made on the basis of the data for pure orthoferrite and orthochromites, and the data for $EuFeO_3$ establish the relative signs of the s.t.h.f.s beyond any doubt.

Substitution by Ni^{3+} ($t_{2g}^6e_g^1$, $S = \frac{1}{2}$) and Mn^{3+} ($t_{2g}^3e_g^1$, $S = 2$) both result in a s.t.h.f. which is of the same sign as that for

Fe^{3+} ($t_{2g}^3e_g^2$, $S = \frac{5}{2}$). These ions are of interest because both have the potential to show a Jahn–Teller distortion. In this respect it was noted that the computer curve-fits for $LaFeO_3$ seemed less satisfactory for these ions, possibly indicating some degree of variation in the s.t.h.f. However, it seemed somewhat surprising that these effects were not greater, and it is possible that the presence of an Sn^{4+} near neighbour has a strong influence over any static distortion.

No attempt was made to include in the correlation the s.t.h.f. at ^{119}Sn with another tin neighbour, as it was felt that the +4 charge on the tin cation and additional compensating Ca^{2+} cation would introduce new factors which were absent when all the substituents were M^{3+} cations.

Conclusions

Magnetic exchange interactions in solid solutions of rare-earth-metal perovskites can be conveniently studied *via* the s.t.h.f. interaction at Sn^{4+} impurity cations. The s.t.h.f. at ^{119}Sn with an environment of six Fe^{3+} nearest-neighbour cations is almost independent of the other substituent cation, but is very strongly dependent on the rare-earth-metal cation. However, the s.t.h.f. at ^{119}Sn with an environment of five Fe^{3+} and one M^{3+} nearest-neighbour cations is also dependent on the radius of the M^{3+} cation and any intrinsic s.t.h.f. which it may produce. Thus it has been possible to show that Cr^{3+}, Mn^{3+}, and Ni^{3+} substituents in rare-earth-metal orthoferrites produce a s.t.h.f. contribution at ^{119}Sn which has the same sign as that produced by the Fe^{3+} cations of the host. It has been found that any s.t.h.f. produced by more distant neighbouring cations is negligible.

Acknowledgements

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