A Mössbauer Study of Rare-earth Metal Pyrochlores A_2FeSbO_7 (A = Lu, Er, Tb, or Sm) using the 37.2-keV γ-Ray of Antimony-121

By **Timothy J. Snee** and **Roy E. Meads,*** Department of Physics, University of Exeter, Exeter EX4 4QL
Frank W. D. Woodhams, Department of Natural Philosophy, University of Aberdeen, Aberdeen AB9 2UE

Isomer shifts and quadrupole splittings have been obtained from the ^{121}Sb Mössbauer spectra of four members of the pyrochlore series A_2FeSbO_7 (A = Lu, Er, Tb, or Sm). The isomer shift (i.s.) decreases linearly with $r(A^{3+})$, the radius of the rare-earth metal ion, and is in the opposite sense to that previously found for the ^{57}Fe i.s. in the same series. This result is interpreted in terms of a decrease in the covalent character of the Sb–O bonds as the distortion of the SbO_6 octahedron increases. The quadrupole-splitting results are of insufficient precision to show any clear trends.

THE crystallographic and ^{57}Fe Mössbauer parameters of the pyrochlore series A_2FeSbO_7 (A = rare-earth metal) have been recorded and discussed in an earlier paper.[1] In the pyrochlore structure the Fe and Sb atoms randomly occupy trigonally distorted octahedral B sites with the distortion decreasing with increasing radius of the rare-earth metal ion, $r(A^{3+})$. This work was extended by that of Ayasse[2] who studied also the stannate series $A_2Sn_2O_7$ by ^{119m}Sn Mössbauer spectroscopy. Mössbauer data on the stannates has also been published by Belyaev *et al.*[3] and by Loebenstein *et al.*[4] Several correlations have been established between the quadrupole splitting (q.s.) and isomer shifts (i.s.) in these compounds and $r(A^{3+})$ or the positional parameter $x(O_2)$ of the 48(f) oxygen anions. $x(O_2)$ and the cubic lattice parameter a_0 are sufficient to define all the ionic positions in the pyrochlore structure (space group $Fd3m$).

The present work was undertaken to see whether

---

[1] O. Knop, F. Brisse, R. E. Meads, and J. Bainbridge, *Canad. J. Chem.*, 1968, **46**, 3829.

[2] C. Ayasse, Ph.D. Thesis, Dalhousie University, Halifax, Nova Scotia, 1972.

[3] L. M. Belyaev, I. S. Lyubutin, L. M. Dem'yanets, T. V. Dmitrieva, and L. P. Matina, *Soviet Phys.* (*Solid State*), 1969, **11**, 424.

[4] H. M. Loebenstein, R. L. Zilber, and H. Zmora, *Phys. Letters*, 1970, **A33**, 453.

similar correlations exist between the q.s. and i.s. of ^{121}Sb in the iron antimonates and the radius of the rare-earth metal $r(A^{3+})$. The experiments were carried out on the compounds for which A = Lu, Er, Tb, and Sm.

EXPERIMENTAL

The method of preparation of the iron antimonates has already been given in detail.[1,2] Mössbauer absorbers were made by enclosing the powder in Perspex holders, each absorber having a thickness of *ca.* 10 mg cm^{-2} of antimony. Spectra were recorded using a conventional constant-acceleration Mössbauer spectrometer under conditions of constant source–absorber–detector geometry. Both source and absorber were kept at 77 K. The source used was ^{121m}Sn in a matrix of CaSnO$_3$ with a nominal strength of 1 mCi (New England Nuclear Corporation). All the spectra show a single resonance-absorption dip in the centre of the spectrum with an isomer shift (i.s.) close to that of Sb^{5+} in an oxide environment, as expected. A representative spectrum of the series, that of Sm$_2$FeSbO$_7$, is shown in Figure 1. All the spectra were least-squares fitted to two models: (*a*) a single line and (*b*) eight lines corresponding to the eight lines expected in a pure quadrupole spectrum of ^{121}Sb. In the fits to model (*b*) the line intensities were constrained to be proportional to the squares of the appropriate Clebsch–Gordan coefficients and the linewidths were constrained to be equal. The ratio of the quadrupole moments of the excited and ground states was taken as 1.38 : 1. Both positive and negative starting values of the quadrupole coupling constant eQ_gV_{zz} were tried and, although both fits converged, the negative value always gave the lower χ^2 values. The asymmetry parameter η was assumed to be zero. [See the results of point-charge calculations of electric-field gradient (e.f.g.) due to the distortion of the nearest-neighbour O^{2-} octahedron given in the following section.]

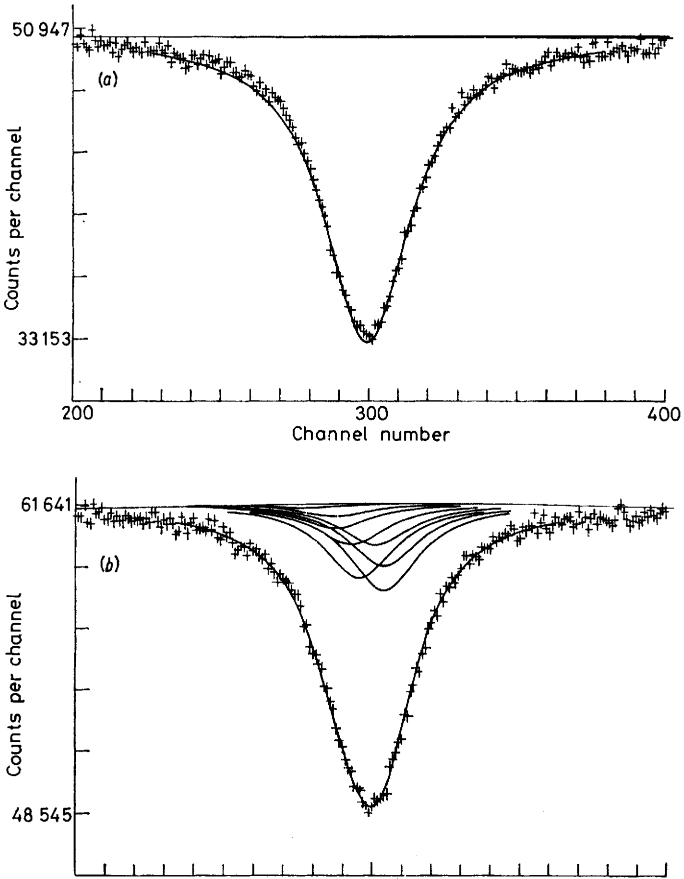

FIGURE 1 Antimony-121 Mössbauer spectra at 77 K of (*a*) Sm$_2$FeSbO$_7$ fitted to a single Lorentzian line, (*b*) Er$_2$FeSbO$_7$ fitted by the eight-line model

The χ^2 values obtained for both fits to models (*a*) and (*b*), with negative eQ_gV_{zz} values, are given in the Table.

Antimony-121 Mössbauer parameters [a] of A$_2$FeSbO$_7$ at 77 K

A	δ	eQ_gV_{zz}	Γ	χ^2 [b] (*a*)	χ^2 [b] (*b*)
Lu	0.132		3.29	203; 216	179; 205
Er	0.102	−6.7	3.49	225; 255	184; 214
Tb	0.058	−6.5	3.54	250; 273	208; 210
Sm	0.014	−6.5	3.39	259; 252	197; 197

[a] δ = Isomer shift relative to CaSnO$_3$ at 77 K ($\pm$0.05 mm s^{-1}); eQ_gV_{zz} = ground-state quadrupole-coupling constant ($\pm$1.0 mm s^{-1}); Γ = linewidth ($\pm$0.05 mm s^{-1}). [b] Refer to fits to models (*a*) and (*b*) respectively (see text). A negative value of e^2qQ_g was used in each type (*b*) fit quoted. A fit using positive e^2qQ_g of the Sm$_2$FeSbO$_7$ spectrum gave χ^2 = 254 and 230.

Since in each experimental run the spectrum was recorded twice, corresponding to positive and negative values of the relative acceleration between source and absorber, the χ^2 values are quoted in pairs. As a lower value of χ^2 was consistently obtained for fits to model (*b*), it may be reasonably concluded that there is a significant, albeit small, quadrupole splitting. The ^{121}Sb Mössbauer parameters obtained from fitting of model (*b*) to the spectra are also given in the Table. The isomer shifts are quoted relative to calcium stannate at 77 K; to convert into InSb add +8.4 mm s^{-1}.

RESULTS AND DISCUSSION

Although the precision of values for the ^{121}Sb quadrupole splitting (q.s.) obtained in the present experiments is insufficient to show any definite trend with the radius of the rare-earth metal $r(A^{3+})$, it seems firmly established that the sign of e^2qQ_g is negative. Because of the negative value (−0.28) for Q_g in ^{121}Sb, the result requires a positive value for the V_{zz} component of the nuclear e.f.g. tensor. Using a point-charge model, the e.f.g. at a B site in the pyrochlore structure due to the nearest-neighbour octahedron of O^{2-} ions can be calculated in terms of the $x(O_2)$ parameter x and the cubic lattice parameter a_0. The results are (1) and (2). The charge

$$V_{zz} = \frac{-3(16x - 7)}{32\pi\varepsilon_0 {a_0}^3[(\frac{1}{2} - x)^2 + \frac{1}{32}]^{\frac{5}{2}}} \tag{1}$$

$$V_{xx} = V_{yy} = \frac{3(16x - 7)}{64\pi\varepsilon_0 {a_0}^3[(\frac{1}{2} - x)^2 + \frac{1}{32}]^{\frac{5}{2}}} \tag{2}$$

on each O^{2-} has been assumed to be −2e and the polarizability of the ions has been ignored. A positive sign for the V_{zz} component of the nuclear e.f.g. tensor would be expected from this calculation provided that: (*a*) the nuclear e.f.g., including the valence contribution, has the same sign as the e.f.g. due to the external charges; and (*b*) that x is less than $\frac{7}{16}$. Although extended point-charge calculations by Ayasse[2] have shown that the effects of more remote ions on V_{zz} may not be neglected, the nearest-neighbour contribution is expected to dominate. Values of $x(O_2)$ have been obtained experimentally in a limited number of cases for stannates and iron antimonates by refinement of crystallographic data,[2,5,6] and are indeed found to be significantly lower than $0.4375(\frac{7}{16})$; for example, the value in Lu_2FeSbO_7 is 0.4216. The values of $x(O_2)$ required to give agreement between measured values and point-charge calculations of the q.s. of ^{57}Fe in the iron antimonates are in good agreement with the crystallographically determined values. In the stannates it is possible to establish proportionality between the measured quadrupole splittings and the calculated values.[2] No direct experimental evidence is available for the sign of V_{zz} at ^{119m}Sn in the stannates.

The results obtained by Ayasse[2] show a linear decrease of ^{57}Fe q.s. with increasing $r(A^{3+})$ in the iron antimonate series at both room temperature and 77 K. At room temperature the values range from 1.01 mm s^{-1} for the lutetium compound to 0.79 mm s^{-1} for that of Eu. The corresponding range at 77 K is from 1.04 to 0.84 mm s^{-1}. The behaviour of the iron antimonates having $A_2 = Nd_2$, Pr_2, or LaPr deviated from the above linear variation. This anomaly is explained by the presence of an impurity orthoferrite phase. Ayasse[2] found also a linear variation with $r(A^{3+})$ of the q.s. at ^{119m}Sn sites in the stannates. At room temperature the measured range is from 0.79 mm s^{-1} at Lu to 0.44 mm s^{-1} at La. At room temperature the results range from 0.82 mm s^{-1} at Yb to 0.46 mm s^{-1} at La. The q.s. data at 77 K for the stannates obtained by Loebenstein *et al.*[4] show consistently higher values. The reason for this is not clear but may be due to the use of rather thick absorbers.[7] At 77 K, quadrupole splittings for both pyrochlore series extrapolate to zero at a value of $r(A^{3+})$ of *ca.* 1.33 Å. This decrease of the quadrupole splittings with increasing $r(A^{3+})$ is consistent with the decreasing trigonal distortion from octahedral symmetry of the B site.

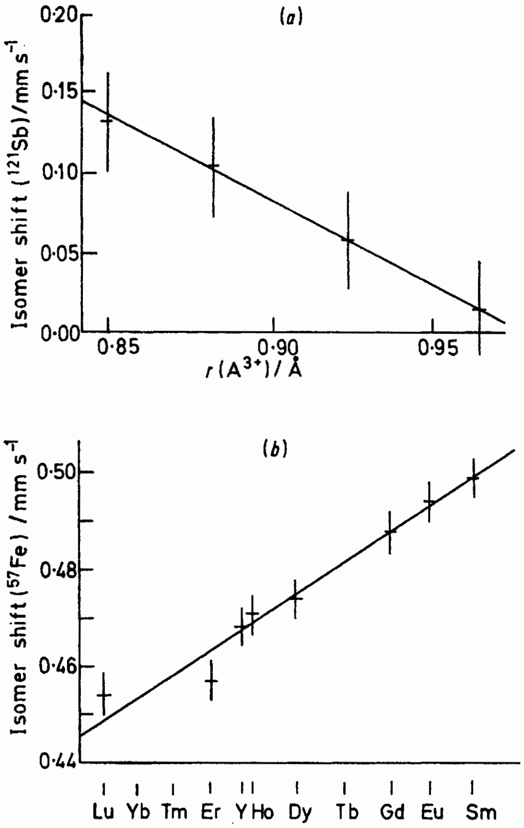

FIGURE 2 Variations of isomer shift with $r(A^{3+})$ in A_2FeSbO_7: (*a*) ^{121}Sb; (*b*) ^{57}Fe

Figure 2(*a*) shows a plot of the ^{121}Sb i.s. against $r(A^{3+})$ for the four pyrochlores studied, and shows convincingly that the i.s. decreases with $r(A^{3+})$. This is quite unlike the variation obtained at both room temperature and 77 K for ^{57}Fe in the iron antimonates[2] where the i.s. increases with $r(A^{3+})$, as shown in Figure 2(*b*). Now an increase in the ^{57}Fe i.s. corresponds to a decrease in *s*-electron density at the iron nucleus. Ayasse[2] argued that this decrease of *s*-electron density with $r(A^{3+})$ is consistent with what would be expected from the simple σ-bonding covalent model: increase in the Fe–O separation with increasing $r(A^{3+})$ will lead to an increase in the ionicity of the bond, and a decrease in the covalent donation to the 4*s* orbital of the Fe atom, resulting in a decrease in *s*-electron density at the Fe nucleus, as observed. Since the sign of the change in the nuclear radius ΔR between the ground and the first excited state is the same for both ^{57}Fe and ^{121}Sb, this simple σ-bonding model predicts the variation of the ^{57}Fe and ^{121}Sb isomer shifts with $r(A^{3+})$ to be similar since Fe and Sb occupy identical sites in the A_2FeSbO_7 lattice. This is inevitably an oversimplified view since the charge-density calculations of Ruby *et al.*[8] show that, for antimony, whilst the addition of 5*s* electrons increases the *s*-electron density at the nucleus, addition of 5*p* electrons will decrease it. However, the change in 5*p* density must be much more marked if it is to produce the same effect as a change in 5*s* density, so that an increase in σ covalency will still generally cause a decrease in the i.s. at ^{121}Sb. This has also been demonstrated by Brukhanov *et al.*[9] who showed that in a series of octahedrally co-ordinated antimony(V) compounds the

---

[5] O. Knop, F. Brisse, L. Castelliz, and Sutarno, *Canad. J. Chem.*, 1965, **43**, 2812.

[6] F. Brisse and O. Knop, *Canad. J. Chem.*, 1968, **46**, 859.

[7] R. E. Meads, B. M. Place, F. W. D. Woodhams, and R. C. Clark, *Nuclear Instr. Methods*, 1972, **98**, 29.

[8] S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, *Phys. Rev.*, 1967, **159**, 239.

[9] V. A. Brukhanov, B. Z. Iofa, V. Kotkhekar, S. I. Semenov, and V. S. Shpinel, *Zhur. eksp. teor. Fiz.*, 1967, **53**, 1582.

i.s. at ^{121}Sb decreases with decreasing electronegativity difference between Sb and the ligand atoms. Moreover, in the present series of compounds, the relative constancy of the Sb q.s. implies that the $5p$ density remains reasonably constant through the series.

Thus the fact that the ^{121}Sb i.s. trend is in the opposite sense to that of ^{57}Fe indicates that there must be at least one other contribution to the s-electron density which varies in the opposite sense to the σ-bonding contribution through the series. In Sb this second contribution must dominate the σ-bonding contribution so that the s-electron density increases through the series with $r(\mathrm{A}^{3+})$. This second contribution could arise in the following manner. So far we have not found it necessary to consider the trigonal distortion of the B-site oxygen octahedron. The q.s. of the high-spin Fe^{3+} ion (and to a limited extent the Sn^{4+} ion) is of course an accurate measure of this distortion which decreases with increasing $r(\mathrm{A}^{3+})$. Now as the distortion of this octahedron is reduced as $r(\mathrm{A}^{3+})$ changes there will be increased overlap of the Sb and O orbitals which will lead to a greater degree of covalency. This in turn will give rise to an increase in $5s$ density on the Sb ion. If this increase outweighs the decrease expected from the increase in bond length, then the i.s. will decrease with increasing $r(\mathrm{A}^{3+})$, as observed.

Covalency effects of Sn–O bonds are expected to be intermediate between those of Fe–O and Sb–O bonds, since the polarizing power of the metal ions increases in the order Fe $<$ Sn $<$ Sb, so that it is tempting to conclude that the relative constancy of the $^{119\mathrm{m}}$Sn i.s. arises from a cancellation of the effects due to bond-length and distortion changes. Very precise measurements of the $^{119\mathrm{m}}$Sn isomer shifts would be required to decide with certainty whether the gradient of the variation with $r(\mathrm{A}^{3+})$ is positive or negative.

We thank Professor O. Knop of the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, for initiating, and for his continued interest in, the work on pyrochlore oxides, Professor O. Knop and Dr. C. Ayasse for the preparation of some of the samples and for instruction in the technique of preparation, Dr. K. C. Moss of the Department of Chemistry, University of Exeter, for helpful discussions, and the S.R.C. for the award of a Research Studentship (to T. J. S.).

[7/351 *Received, 28th February*, 1977]
