

UNIVERSITY OF BIRMINGHAM

Research at Birmingham

57Fe Mössbauer spectra from fluorinated phases of Fe_{0.50}M_{0.50}(M=Co,Mg)Sb₂O₄

Berry, Frank J.; De Laune, Benjamin P.; Greaves, Colin; Thomas, Michael F.; Jumas, Jean-claude

DOI:

[10.1007/s10751-019-1621-8](https://doi.org/10.1007/s10751-019-1621-8)

License:

Creative Commons: Attribution (CC BY)

Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Berry, FJ, De Laune, BP, Greaves, C, Thomas, MF & Jumas, J 2019, '57Fe Mössbauer spectra from fluorinated phases of Fe_{0.50}M_{0.50}(M=Co,Mg)Sb₂O₄', *Hyperfine Interactions*, vol. 240, no. 1, 77.
<https://doi.org/10.1007/s10751-019-1621-8>

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.



^{57}Fe Mössbauer spectra from fluorinated phases of $\text{Fe}_{0.50}\text{M}_{0.50}(\text{M} = \text{Co}, \text{Mg})\text{Sb}_2\text{O}_4$

Frank J. Berry¹ · Benjamin P. de Laune¹ · Colin Greaves¹ · Michael F. Thomas² · Jean-Claude Jumas³

Published online: 27 June 2019
© The Author(s) 2019

Abstract

Fluorinated phases formed by reaction of $\text{Fe}_{0.5}\text{Co}_{0.5}\text{Sb}_2\text{O}_4$ and $\text{Fe}_{0.5}\text{Mg}_{0.5}\text{Sb}_2\text{O}_4$ with gaseous fluorine have been examined by ^{57}Fe Mössbauer spectroscopy between 298 and 5 K. The degree of oxidation of Fe^{2+} to Fe^{3+} has been used to quantify the amount of fluorine incorporated within the channels of the schafarzikite-related structure and enable the evaluation of the compositions as $\text{Fe}_{0.5}\text{Co}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.41}$ and $\text{Fe}_{0.5}\text{Mg}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.31}$. The multiplicity of components observed in the spectra recorded in the paramagnetic regime can be related to the number of near neighbour fluoride ions which lie in the channels at the same value of the crystal z -coordinate as the iron ions. Comparison of the magnetically ordered spectra recorded at lower temperatures from $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.41}$ with those recorded previously from FeSb_2O_4 indicates that the insertion of fluoride ions into the channels of the structure does not affect the angle between the EFG and magnetic hyperfine field.

Keywords Schafarzikite · Fluorinated oxides · Mössbauer spectroscopy

1 Introduction

The insertion of fluorine into two-dimensional structures induces structural changes and electronic properties resulting from the oxidation of metal ions in the host material. The conversion of semiconducting La_2CuO_4 to superconducting $\text{La}_2\text{CuO}_4\text{F}_x$ [1] illustrates this type of reaction and other examples are documented in a recent review [2]. As a part of our

This article is part of the Topical Collection on *Proceedings of the 5th Mediterranean Conference on the Applications of the Mössbauer Effect (MECAME 2019) and 41st Workshop of the French-speaking Group of Mössbauer Spectroscopy (GFSM 2019), Montpellier, France, 19-23 May 2019*
Edited by Pierre-Emmanuel Lippens, Yann Garcia, Moulay-Tahar Sougrati and Mira Ristic (†)

✉ Frank J. Berry
f.j.berry.1@bham.ac.uk

¹ School of Chemistry, The University of Birmingham, Birmingham B15 2TT, UK

² Department of Physics, University of Liverpool, Liverpool L69 3BX, UK

³ Institut Charles Gerhardt (UMR 5253), Université Montpellier, Case Courrier 1502, Place Eugene Bataillon, 34095 Montpellier Cedex 5, France

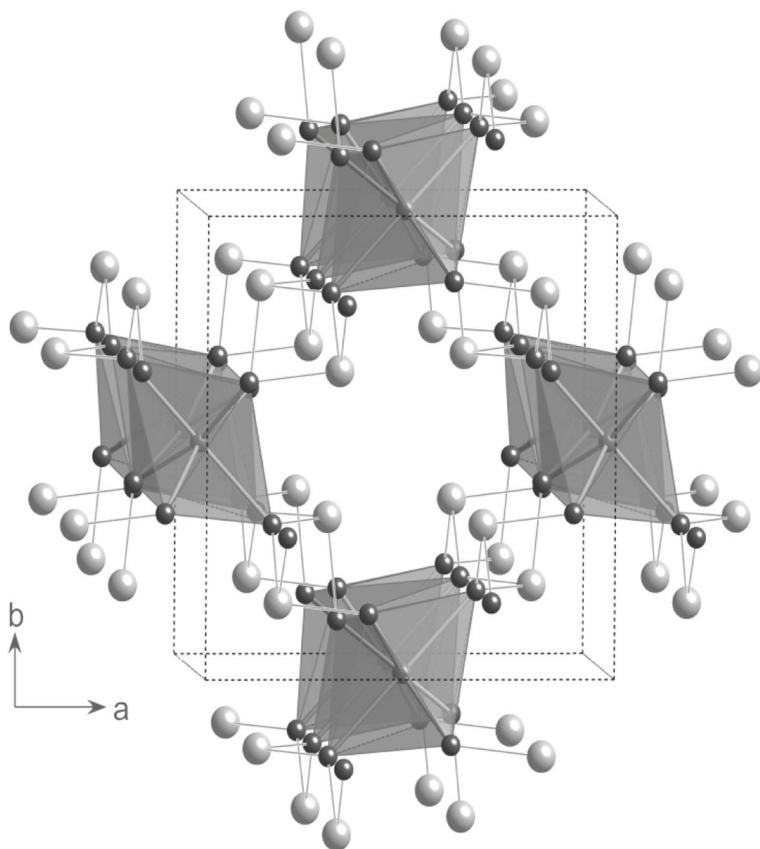


Fig. 1 The structure of FeSb_2O_4 : FeO_6 octahedra are shaded with Fe^{2+} ions located within the octahedra; O^{2-} ions are shown as black spheres and Sb^{3+} ions are shown as white spheres

ongoing interest in the fluorination of inorganic structures we have recently reported on the accommodation of fluorine within the narrow one-dimensional channels of phases related to the mineral schafarzikite of composition FeSb_2O_4 [3].

The compound FeSb_2O_4 is isostructural with the tetragonal form of Pb_3O_4 [4, 5] (Fig. 1) and consists of rutile-related chains of FeO_6 octahedra along the c -axis linked by trigonal pyramidal Sb^{3+} cations which, being bound to three oxygen anions, possess a lone pair of electrons which can be regarded as a fourth ligand. The Fe-Fe distance within the chains (2.96 Å) is shorter than the nearest Fe-Fe distance within the layers (6.07 Å) and is consistent with the one-dimensional character of FeSb_2O_4 . The material undergoes an antiferromagnetic transition around 45 K [6, 7]. The ^{57}Fe Mössbauer spectrum of FeSb_2O_4 at ca. 4.2 K is unusual, being the result of combined magnetic hyperfine and electric quadrupole interactions of comparable strength [8–10] and, together with data recorded above T_N [11], has been used to determine the order of the t_{2g} orbital energy levels. The literature also documents some structurally related compounds of composition MSb_2O_4 ($\text{M} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mg}^{2+}$) [12–17].

We have also prepared new phases involving substitution on the M site. The magnetic properties deduced from neutron diffraction, magnetic susceptibility and Mössbauer spectroscopy measurements in the series of composition $\text{Fe}_{1-x}\text{Co}_x\text{Sb}_2\text{O}_4$ suggested the existence of some short range correlations within the chains [18, 19] whilst in materials of formulation Fe_1

$_{-x}\text{Mg}_x\text{Sb}_2\text{O}_4$, the decrease in magnetic ordering temperature with increasing concentrations of magnesium was associated with non-magnetic Mg^{2+} ions weakening the magnetic interactions between Fe^{2+} ions [19, 20]. We have also demonstrated the capacity of these materials to accommodate additional oxygen within their structures [21].

Our previous work [3] reported on the reaction of $\text{Mg}_{0.50}\text{Fe}_{0.50}\text{Sb}_2\text{O}_4$ and $\text{Co}_{0.50}\text{Fe}_{0.50}\text{Sb}_2\text{O}_4$ with fluorine gas at low temperatures to give topotactic insertion of fluorine into the channels which are an inherent feature of the structure. Neutron powder diffraction and solid state NMR studies showed that the interstitial fluoride ions were bound to antimony within the channel walls to form $\text{Sb}-\text{F}-\text{Sb}$ bridges. ^{57}Fe Mössbauer spectra recorded at 300 K showed that oxidation of Fe^{2+} to Fe^{3+} was primarily responsible for balancing the increased negative charge associated with the presence of the fluoride ions within the channels.

In this work we report on the ^{57}Fe Mössbauer spectra recorded at low temperatures from new samples of the fluorinated phases of $\text{Mg}_{0.50}\text{Fe}_{0.50}\text{Sb}_2\text{O}_4$ and $\text{Co}_{0.50}\text{Fe}_{0.50}\text{Sb}_2\text{O}_4$ with the schafarzikite structure and their interpretation in terms of the number of near F^- ions which lie in the channels at the same value of the crystal z -coordinate as the iron ions and the magnetic properties of these materials.

2 Experimental

Materials of composition $\text{Mg}_{0.50}\text{Fe}_{0.50}\text{Sb}_2\text{O}_4$ and $\text{Co}_{0.50}\text{Fe}_{0.50}\text{Sb}_2\text{O}_4$ were prepared by heating appropriate quantities of the dried metal oxides in evacuated sealed quartz tubes as previously described [18, 20]. Fluorinated samples were obtained by heating the parent oxides in flowing fluorine gas (10% in nitrogen) at 230°C and purging with gaseous nitrogen or argon [3]. The structural characterisation and analysis of the samples of composition $\text{Fe}_{0.5}\text{Co}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.49}$ and $\text{Fe}_{0.5}\text{Mg}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.31}$ has been reported previously [3]. In this work new samples were examined.

^{57}Fe Mössbauer spectra were recorded in a helium gas-flow cryostat in constant acceleration mode using a ca. 25 mCi ^{57}Co source. All spectra were computer fitted and all chemical isomer shift data are quoted relative to metallic iron at room temperature.

3 Results and discussion

3.1 $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_x$

The ^{57}Fe Mössbauer spectra recorded at 298 K, 80 K, 45 K, 20 K and 5 K are shown in Fig. 2 and the fitting parameters are listed in Table 1. The spectra are different from those reported previously [3] which is not unexpected given that we have already noted [3] that differences in fluorine content probably relates to differences in particle size of starting materials and the fluorination conditions not being identical.

3.1.1 Formula of $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_x$

Our initial analysis of the ^{57}Fe Mössbauer spectra was directed towards the evaluation of x and hence the formula of the material examined here. The spectrum recorded at 80 K shows the ratio of the combined Fe^{2+} components (with $\delta = 1.34\text{mms}^{-1}$) to the Fe^{3+} component (with $\delta =$

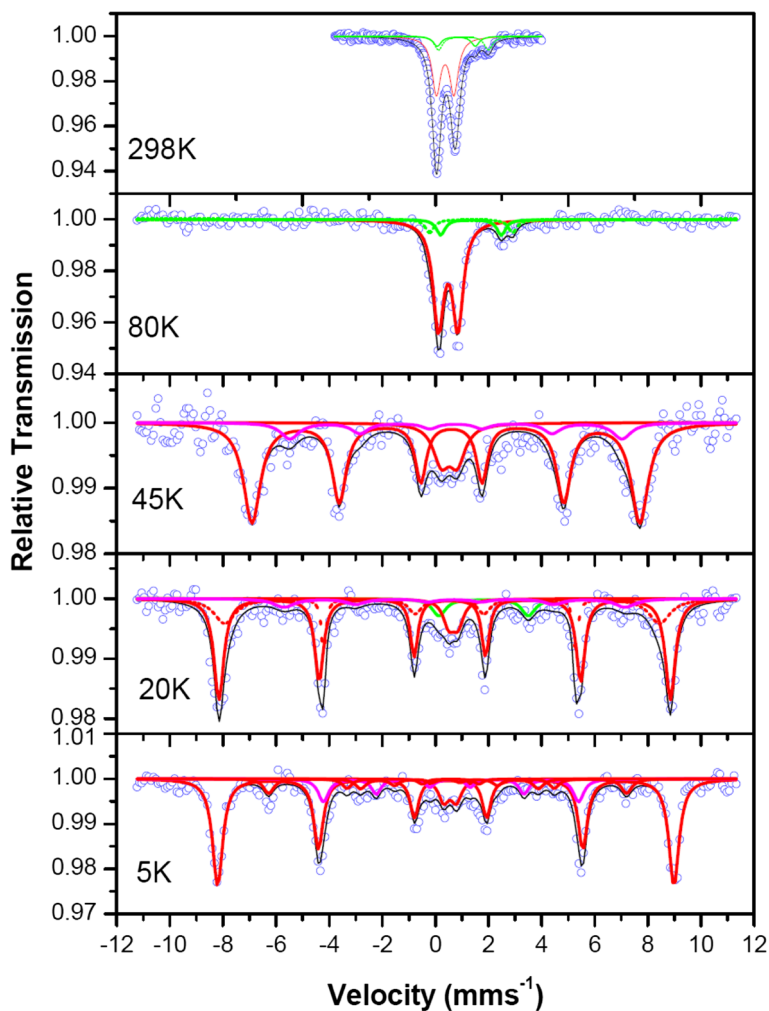


Fig. 2 ^{57}Fe Mössbauer spectra recorded from $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.41}$

0.48 mms^{-1}) to be 18: 82. Assuming charges of Co^{2+} , Sb^{3+} , and O^{2-} we calculate a value of $x = 0.41$ and hence a formula of $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.41}$.

3.1.2 Identification of components in spectra recorded at 298 K and 80 K

The spectrum recorded at 298 K showed a component with $\delta = 1.06 \text{ mms}^{-1}$ which can readily be assigned to Fe^{2+} and components with $\delta = 0.41 \text{ mms}^{-1}$ and $\delta = 0.37 \text{ mms}^{-1}$ characteristic of Fe^{3+} (the partial superposition of the two components precludes their observation in Fig. 2). The small (ca. 7%) component with isomer shift $\delta = 0.79 \text{ mms}^{-1}$ is intermediate between the isomer shift values for Fe^{2+} and Fe^{3+} . We assign this to an intermediate charge state related to some electron -delocalisation or -hopping of electrons between Fe^{2+} and Fe^{3+} ions. At 80 K and at lower temperatures this behaviour disappears as expected and the spectral components can be assigned as Fe^{2+} and Fe^{3+} .

Table 1 ^{57}Fe Mössbauer parameters recorded from $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.41}$

Temperature (K)	$\delta \pm 0.02(\text{mm s}^{-1})$	Δ or $e^2qQ/2 \pm 0.02(\text{mm s}^{-1})$	$H \pm 0.5$ (T)	$LW \pm 0.02$ (mm s^{-1})	Area $\pm 5\%$
298	1.06	1.89	–	0.36	10
	0.79	1.44	–	0.38	7
	0.41	0.77	–	0.39	41
	0.37	0.66	–	0.39	42
80	1.34	3.12	–	0.39	8
	1.34	2.28	–	0.39	10
	0.48	0.73	–	0.48	82
45	0.50	–0.22	45.3	0.80	75
20	0.50	–0.20	52.8	0.50	60
5	0.50	–0.16	53.4	0.46	64

The fitting parameters listed in Table 1 show that in the spectrum recorded at 298 K the two Fe^{3+} components have slightly different values of quadrupole splitting. In the spectrum recorded at 80 K there are two Fe^{2+} components with slightly different values of quadrupole splitting. We have investigated whether this behaviour could be linked to different near neighbour fluoride configurations around the iron ions.

In the ab -planes containing the iron- and fluoride- ions the structure [3] shows that there are four possible sites for an inserted fluoride ion around each iron ion. A simulation incorporating random occupation by iron and cobalt of the cation sites and random occupation of surrounding fluoride sites (subject to their relative abundance, x) indicated that the relative percentages of an iron ion having 0,1,2,3 near neighbour fluoride ions was 9%, 42%, 42% and 7% respectively. This provides some indication that the observed difference in splitting in the doublets observed in spectra recorded in the paramagnetic regime corresponds to the main probabilities of having 1 or 2 fluoride neighbours.

3.1.3 Spectra recorded at 45 K, 20 K and 5 K

The spectra recorded below 80 K all show the superposition of magnetic sextet components. This is consistent with a magnetic ordering temperature $T_N = 75$ K recorded from magnetisation results recorded previously from the compound $\text{Fe}_{0.5}\text{Co}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.49}$ [3]. Despite their complexity each spectrum is clearly dominated by a sextet of large spectral area with isomer shift characteristic of Fe^{3+} . We associate these sextet components as the low temperature versions of the large-area Fe^{3+} doublet components observed in the spectra recorded at 298 K and 80 K. In these sextet spectra the quadrupole shift Δ is evaluated from $2\Delta =$ the energy difference between the splitting of lines 5 and 6 and lines 1 and 2 of the sextet. The angle Θ between the principal axis of the electric field gradient (EFG) and the direction of the magnetic hyperfine field B_{hf} can be evaluated from the values of Δ and the quadrupole splitting $e^2qQ/2$ observed in the 80 K spectrum using the relation

$$\Delta = e^2qQ/2 \cdot \frac{1}{2} \cdot (3\cos^2\Theta - 1).$$

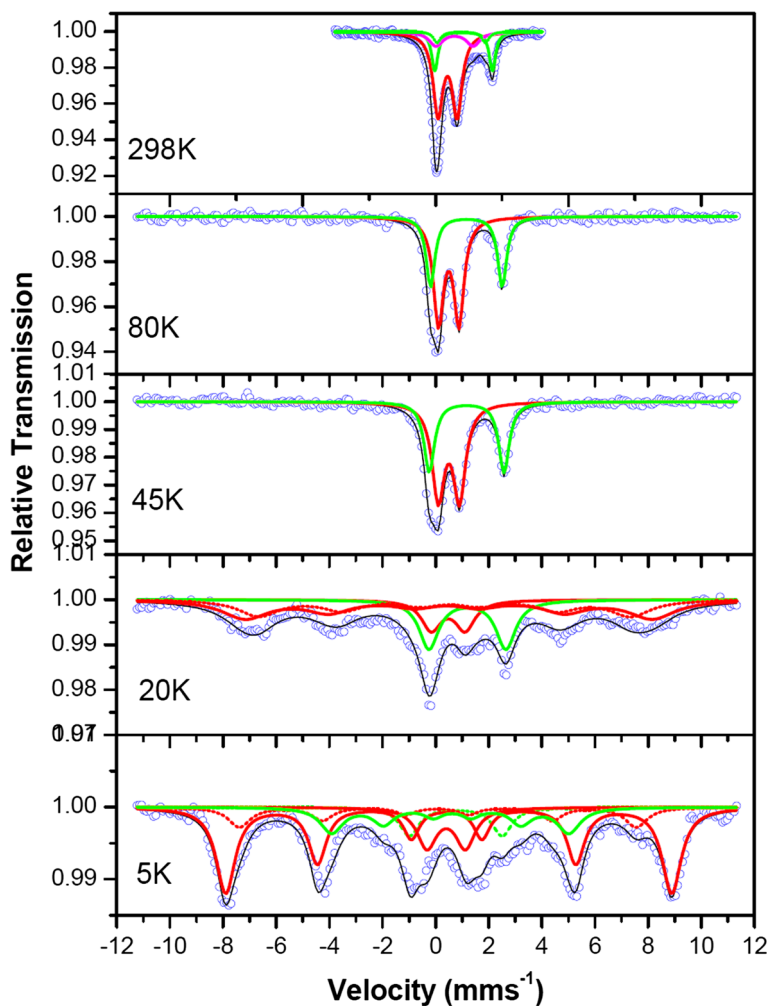


Fig. 3 ^{57}Fe Mössbauer spectra recorded from $\text{Fe}_{0.5}\text{Mg}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.31}$

The values of Θ from the spectra at 45 K, 20 K and 5 K are evaluated as 69° , 67° and 64° respectively. These values are effectively identical to those measured in the parent material FeSb_2O_4 [10] and although there are differences – in FeSb_2O_4 the iron is Fe^{2+} and the magnetic structure is A- type instead of the present C- type – it seems that the insertion of fluoride ions into the channels of the structure does not affect the angle between EFG and magnetic hyperfine field. Given the complexity of the Fe^{2+} spectral components we have not analysed these to a degree which justifies inclusion of parameters in Table 1.

3.2 $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_x$

The ^{57}Fe Mössbauer spectra recorded at 298 K, 80 K, 45 K, 20 K and 5 K are shown in Fig. 3 and the fitting parameters are listed in Table 2.

Table 2 ^{57}Fe Mössbauer parameters recorded from $\text{Fe}_{0.5}\text{Mg}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.31}$

Temperature (K)	$\delta \pm 0.02(\text{mm s}^{-1})$	Δ or $e^2qQ/2 \pm 0.02(\text{mm s}^{-1})$	$H \pm 0.5$ (T)	$\text{LW} \pm 0.02$ (mm s^{-1})	$\text{Area} \pm 5\%$
298	1.05	2.17	–	0.29	20
	0.97	1.82	–	0.32	5
	0.71	1.40	–	0.63	15
	0.45	0.72	–	0.44	60
80	1.16	2.70	–	0.40	37
	0.49	0.77	–	0.46	63
45	1.17	2.81	–	0.48	39
	0.50	0.80	–	0.56	61
20	1.20	2.89	–	0.90	22
	0.46	0.04	47.6	2.10	37
5	0.44	–0.10	43.5	1.80	28
	0.46	0.04	52.1	0.90	49

3.2.1 Formula of $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_x$

The spectrum recorded at 80 K shows the ratio of the areas corresponding to the components assigned as Fe^{2+} and Fe^{3+} to be 37: 63. Application of the approach described in 3.1.1 above, and assuming the presence of Mg^{2+} , translates to a value of $x = 0.31$ and corresponds to a formula of $\text{Mg}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.31}$.

3.2.2 Identification of components

The spectra recorded at 80 K and 45 K are well fitted with a single Fe^{3+} quadrupole split component and a single Fe^{2+} quadrupole split component.

The spectrum recorded at 298 K spectrum shows- in addition to the Fe^{3+} and Fe^{2+} quadrupole split components- a component with isomer shift $\delta = 0.71 \text{ mms}^{-1}$ which, as in $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.41}$, can be associated with electron mobility between Fe^{2+} and Fe^{3+} ions. At lower temperatures this component is not observed as electrons become localised on the Fe^{2+} and Fe^{3+} ions.

A simulation similar to that described in 3.1.2 above was performed – with $x = 0.31$. This indicated that the percentages of iron ions having 0,1 and 2 near neighbour fluoride ions is 25%, 50%, 25%. This distribution appears not to cause observable differences in quadrupole splitting for the Fe^{3+} components in the 298 K, 80 K and 45 K spectra or for the Fe^{2+} components in the 80 K and 45 K spectra.

3.2.3 Spectra at 20 K and 5 K

The spectra at 20 K and 5 K both show components representing magnetically ordered and non-ordered states of Fe^{2+} and Fe^{3+} ions. However, these components are not sufficiently well defined to enable the evaluation of the angle theta or further analysis. In particular the complexity of the Fe^{2+} spectral components precluded confident evaluation of parameters for inclusion in Table 2.

4 Conclusion

The ^{57}Fe Mössbauer spectra recorded from fluorinated $\text{Mg}_{0.50}\text{Fe}_{0.50}\text{Sb}_2\text{O}_4$ and $\text{Co}_{0.50}\text{Fe}_{0.50}\text{Sb}_2\text{O}_4$ show that a major effect of fluoride ion insertion involves the oxidation of

Fe^{2+} ions to Fe^{3+} ions in the structure. The ^{57}Fe Mössbauer spectra enable the degree of fluorination to be evaluated and the compositions to be derived. We suggest that the multiplicity of components in the spectra recorded in the paramagnetic regime may be related to the number of near fluoride ions which lie in the channels at the same value of the crystal z -coordinate as the iron ions. Comparison of the magnetically ordered spectra recorded at lower temperatures from $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Sb}_2\text{O}_4\text{F}_{0.41}$ with those recorded previously from FeSb_2O_4 indicates that the insertion of fluoride into the channels of the structure does not affect the angle between EFG and magnetic hyperfine field.

Acknowledgments We thank the Engineering and Science Research Council for financial support of this research (EPSRC EP/L014114/1).

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Chevalier, B., Tressaud, A., Lepine, B., Amine, K., Dance, J.M., Lozano, L., Hickey, E., Etourneau, J.: Stabilization of a new superconducting phase by low temperature fluorination of La_2CuO_4 . *Physica C*. **167**, 97–101 (1990)
- Slater, P.R., Driscoll, L.: Photonic and Electronic Properties of Fluoride Materials. In: Tressaud, A. (ed.) Poppelmeier, Progress in Fluorine Science Series Vol 1, pp. 401–421. Elsevier, Amsterdam (2016) Modification of Magnetic and Electronic Properties, in Particular Superconductivity, by Low Temperature Insertion of Fluorine into Oxides
- De Laune, B.P., Rees, G.J., Marco, J., Hah, H.-Y., Johnson, C.E., Johnson, J.A., Berry, F.J., Hanna, J.V., Greaves, C.: Topotactic Fluorine Insertion into the Channels of FeSb_2O_4 -Related Materials. *Inorg. Chem.* **56**, 10078–10089 (2017)
- Gavarrí, J.R., Vigouroux, J.P., Calvarin, G., Hewat, A.W.: Structure de SnPb_2O_4 à quatre températures: relation entre dilatation et agitation thermiques. *J. Solid State Chem.* **36**, 81–90 (1981)
- Fischer, R., Pertlik, F.: Tschermarks Miner. *Petrogr. Mitt.* **22**, 236–241 (1975)
- Gonzalo, J.A., Cox, D.E., Shirane, G.: The Magnetic Structure of FeSb_2O_4 . *Phys. Rev.* **147**, 415–418 (1966)
- Chater, R., Gavarrí, J.R., Hewat, A.W.: Structures isomorphes MeX_2O_4 —Evolution structurale entre 2 K et 300 K de l'antimonite FeSb_2O_4 : Elasticité et ordre magnétique anisotropes. *J. Solid State Chem.* **60**, 78–86 (1985)
- Varret, F., Imbert, P., Gerard, A., Hartmann-Boutron, F.: Etude de FeSb_2O_4 par effet Mössbauer. *Solid State Commun.* **6**, 889–892 (1968)
- Petit, G., Meder, M.R.: ^{57}Fe Mossbauer spectra from FeSb_2O_4 *Hyperfine Interact.* **5**, 323 (1978)
- Bayliss, R.D., Berry, F.J., de Laune, B.P., Greaves, C., Helgason, O., Marco, J.F., Thomas, M.F., Vergara, L., Whitaker, M.J.: Magnetic interactions in ferrous antimonite, FeSb_2O_4 , and some derivatives *J. Phys. Condens. Matter.* **24**, 276001 (2012)
- Eibschutz, M., Ganiél, U.: Mössbauer studies of paramagnetic FeSb_2O_4 . *Solid State Commun.* **6**, 775–777 (1968)
- Tammann, G.: Chemische Reaktionen in pulverförmigen Gemengen zweier Kristallarten. *Z. Anorg. Allg. Chem.* **149**, 21–34 (1925)
- Koyama, E., Nakai, I., Nagashima, K.: Hydrothermal synthesis of a single crystal of FeSb_2O_4 and isostructural compounds *Nippon Kagaku Kaishi.* **6**, 793–795 (1979)
- Gavarrí, J.R., Calvarin, G., Chardon, B.: Composés isomorphes MeX_2O_4 : Dilatation thermique anisotrope et ordre magnétique dans MnSb_2O_4 . *J. Solid State Chem.* **47**, 132–142 (1983)
- Witteveen, H.T.: Magnetic susceptibility of NiAs_2O_4 and NiSb_2O_4 *Solid State Commun.* **9**, 1313–1315 (1971)
- Stähl, S.: The crystal structure of ZnSb_2O_4 and isomorphous compounds *Ark. Khem. Min. Geol.* **17B**, 1–7 (1943)

17. Atanasova, M.T., Strydom, A.M., Schutte, C.J.H., Prinsloo, L.C., Focke, W.W.: Crystal structure and magnetic properties of CuSb_2O_4 . *J. Mater. Sci.* **49**, 3497–3510 (2014)
18. Cumby, J., de Laune, B.P., Greaves, C.: The structures and magnetic properties of $\text{Fe}_x\text{Co}_{1-x}\text{Sb}_2\text{O}_4$ and $\text{Mn}_x\text{Co}_{1-x}\text{Sb}_2\text{O}_4$. *J. Mater. Chem. C.* **4**, 201–208 (2016)
19. Berry, F.J., de Laune, B.P., Greaves, C., Hah, H.-Y., Johnson, C., Johnson, J.A., Kameli, S., Whitaker, M.J., Marco, J.F., Thomas, M.F., Whitaker, M.J.: Magnetic interactions in $\text{Fe}_{1-x}\text{M}_x\text{Sb}_2\text{O}_4$ ($\text{M}=\text{Mg}, \text{Co}$) deduced from Mossbauer spectroscopy. *Hyperfine Interact.* **239**, 31–39 (2018)
20. de Laune, B.P., Whitaker, M.J., Marco, J.F., Thomas, M.F., Berry, F.J., Lees, M.R., Greaves, C.: Synthesis and magnetic characterization of $\text{Fe}_{1-x}\text{Mg}_x\text{Sb}_2\text{O}_4$ ($x=0.25, 0.50, 0.75$) and their oxygen-excess derivatives. *J. Mater. Chem. C.* **5**, 4985 (2017)
21. de Laune, B.P., Rees, G.J., Whitaker, M.J., Hah, H.-Y., Johnson, C., Johnson, J.A., Brown, D.E., Tucker, M.G., Hansen, T.C., Berry, F.J., Hanna, J.V., Greaves, C.: Oxygen insertion reactions within the 1-D channels of phases related to FeSb_2O_4 . *Inorg. Chem.* **56**, 594 (2017)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.