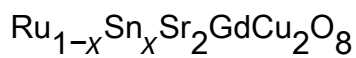


Magnetic interactions on the tin sites in the tin-doped ferromagnetic superconductor



This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 955

(<http://iopscience.iop.org/0953-8984/16/6/022>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 12:42

Please note that [terms and conditions apply](#).

Magnetic interactions on the tin sites in the tin-doped ferromagnetic superconductor $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$

J P Attfield¹, F J Berry^{2,4}, J Bland³, A M Beesley³, A C McLaughlin¹ and M F Thomas³

¹ Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

² Department of Chemistry, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK

³ Department of Physics, University of Liverpool, Liverpool L69 7ZE, UK

Received 12 September 2003

Published 30 January 2004

Online at stacks.iop.org/JPhysCM/16/955 (DOI: 10.1088/0953-8984/16/6/022)

Abstract

The magnetic environment of tin in the ferromagnetic superconductor $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ has been probed by doping ^{119}Sn ions onto the ruthenium sites. The transferred magnetic hyperfine interaction at the tin site was measured by Mössbauer spectroscopy in the temperature range 4.2–300 K. The spectra show two distinct tin sites. One has four ruthenium nearest-neighbour cations and the other three ruthenium and one tin nearest neighbours. The temperature dependence of the hyperfine fields indicates an ordering temperature of 108 ± 5 K. The spectra favour parallel alignment of the field with the major axis of the electric field gradient indicating that the ruthenium moments are aligned along the crystallographic c axis.

1. Introduction

Ferromagnetism and superconductivity are usually mutually exclusive. For example, ErRh_4B_4 has a superconductor critical temperature of 8.7 K but loses its superconducting properties when it ferromagnetically orders at 0.93 K [1]. However, the coexistence of ferromagnetism and superconductivity has recently been reported in the compound $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ [2–9]. The average crystal structure of tetragonal $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (figure 1) is similar to that of other 1212-type cuprate superconductors, consisting of a layer of almost regular RuO_6 octahedra connected through their apices to two layers of CuO_5 square pyramids. The bond mismatch between the in-plane Ru–O and Cu–O bonds leads to rotation of the RuO_6 octahedra around c by 13° at 295 K. A slight tilting of the polyhedra, which reduces the Cu–O–Ru angle to 173° , is also observed [6, 8]. A slight canting of the moments may arise from an antisymmetric (Dzyaloshinsky–Moriya) interaction between neighbouring moments on ruthenium and which is non-zero due to the twists and tilts of the RuO_6 octahedra. This would give rise to an overall magnetic arrangement containing both ferro- and antiferromagnetic components. The

⁴ Author to whom any correspondence should be addressed.

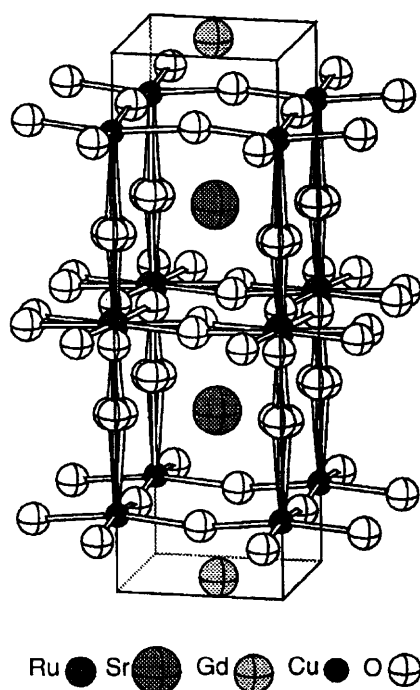


Figure 1. The average crystal structure of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ showing the tilts and rotations of the RuO_6 octahedra.

magnetic ordering at $T_M = 136$ K results from the ordering of moments in the RuO_2 planes and persists through the onset of superconductivity at $T_C = 46$ K to the lowest temperature investigated (1.9 K). The presence of ferromagnetism was confirmed by the observation of hysteresis loops in variable field measurements below T_M . The moments on gadolinium align antiferromagnetically but at much lower temperatures ($T_N = 2.0$ K). More recently, attempts have been made to replace ruthenium by non-magnetic fixed valent cations such as Sn^{4+} [10–12]. The substitution of the larger Sn^{4+} ion for ruthenium was found to increase the bond mismatch between the in-plane Ru–O and Cu–O bonds and to enhance T_C but to suppress T_M and the ferromagnetic moment in the ruthenate layers [10, 12]. We have prepared $\text{Ru}_{0.935}\text{Sn}_{0.065}\text{Sr}_2\text{GdCu}_2\text{O}_8$ containing tin-119 and report here on the examination of the material by ^{119}Sn Mössbauer spectroscopy.

2. Experimental details

The material of composition $\text{Ru}_{0.935}\text{Sn}_{0.065}\text{Sr}_2\text{GdCu}_2\text{O}_8$ was prepared from a ground stoichiometric mixture of RuO_2 , $^{119}\text{SnO}_2$, SrCO_3 , Gd_2O_3 and CuO which was pressed into a pellet and heated in flowing nitrogen at 1010°C (20 h) to minimize the formation of SrRuO_3 . The pellet was furnace-cooled, reground, repelleted and subsequently heated in flowing oxygen at 1050°C (10 h) and at 1055°C (10 h) before annealing at 1060°C under flowing oxygen (4 days) and slowly cooled to room temperature. X-ray powder diffraction showed the tin-doped compound to be a single phase with a tetragonal cell as previously found [12].

^{119}Sn Mössbauer spectra were recorded from the sample at temperatures between 298 and 4.2 K in a helium flow cryostat with a constant acceleration spectrometer using an

Table 1. ^{119}Sn Mössbauer parameters for the three components used to fit the spectra of figures 2 and 3. Components 1 and 2 refer to ^{119}Sn in sites with 4-Ru neighbours and 3-Ru+1-Sn neighbours, respectively, in $\text{Ru}_{0.935}\text{Sn}_{0.065}\text{Sr}_2\text{GdCu}_2\text{O}_8$. Component 3 refers to ^{119}Sn in SrSnO_3 . The errors in the parameters are highly correlated and are based on multiple fit attempts around the quoted values.

Temp. (K)	Component 1					Component 2					Component 3		
	δ (mm s ⁻¹)	Δ (mm s ⁻¹)	B_{hf} (kG)	θ°	A %	δ (mm s ⁻¹)	Δ (mm s ⁻¹)	B_{hf} (kG)	θ°	A %	δ (mm s ⁻¹)	Δ (mm s ⁻¹)	A %
4.2	0.36	-0.51	44.4	0	48	0.40	-1.52	24.8	0	35	0.08	0	17
9.8	0.33	-0.51	44.2	0	52	0.35	-1.50	24.0	0	29	0.07	0	19
18.7	0.30	-0.48	43.8	0	44	0.33	-1.49	23.4	0	37	0.06	0	19
27.8	0.30	-0.57	42.3	0	44	0.33	-1.64	20.9	0	37	0.06	0	19
28.7	0.30	-0.58	41.0	0	44	0.33	-1.72	18.1	0	37	0.06	0	19
48.2	0.30	-0.67	39.4	0	44	0.33	-1.70	17.5	0	37	0.06	0	19
58.7	0.30	-0.68	36.8	0	44	0.33	-1.57	16.4	0	37	0.06	0	19
77	0.33	-1.34	24.1	0	44	0.39	-1.52	12.6	0	37	0.06	0	19
100	0.33	-1.61	14.0	0	44	0.39	-1.51	1.7	0	37	0.07	0	19
150	0.35	0.88	0	0	51	0.36	1.62	0	0	38	0.05	0	11
300	0.32	0.90	0	0	54	0.31	1.57	0	0	35	0.00	0	12

approximately 25 mCi $\text{Ca}^{119}\text{SnO}_3$ source at 298 K. The chemical isomer shift data are quoted relative to SnO_2 at 298 K.

3. Results and discussion

The evolution of the Mössbauer spectra with temperature in the ranges 4.2–50 K and from 50 to 300 K are shown in figures 2 and 3, respectively. While individual spectra are easy to fit, it has proved much more challenging to fit the series of spectra with parameters that varied with temperature in an understandable fashion. The series of fits presented here consist of three components—two show magnetic splitting below 100 K and one shows no magnetic or quadrupole splitting over the entire temperature range. The complete set of parameters used to fit the spectra are listed in table 1. The single peak absorption designated as component 3 can be attributed to the presence of SrSnO_3 [13]. Such an impurity phase has been previously observed by x-ray powder diffraction when the doping level of tin in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ exceeds 10%. Although the doping level of tin in the material investigated here is nominally 6.5% the observation of a component which can be assigned to SrSnO_3 reflects the enhanced sensitivity of ^{119}Sn Mössbauer spectroscopy to the presence of small amounts of tin-containing impurity phases. The ^{119}Sn Mössbauer parameters for component 3 (table 1) showed no magnetic or quadrupole splitting as expected for tin in the octahedral site of SrSnO_3 and an isomer shift of zero at 300 K, which is identical to that of the CaSnO_3 source and which increases as the temperature decreases as a result of the second-order Doppler shift. We estimate that about 19% of the tin is present in the SrSnO_3 impurity.

The sextet patterns designated as components 1 and 2 are associated with tin ions substituting for ruthenium ions in the compound $\text{RuSr}_2\text{GdCu}_2\text{O}_8$. In these sites the tin ions experience a transferred magnetic hyperfine interaction in the ferromagnetic phase from the neighbouring magnetic ruthenium ions. Component 1, with the larger value of the hyperfine magnetic field, B_{hf} , is attributed to a tin ion with four ruthenium nearest cation neighbours. We associate component 2, with the smaller value of the hyperfine magnetic field, with a

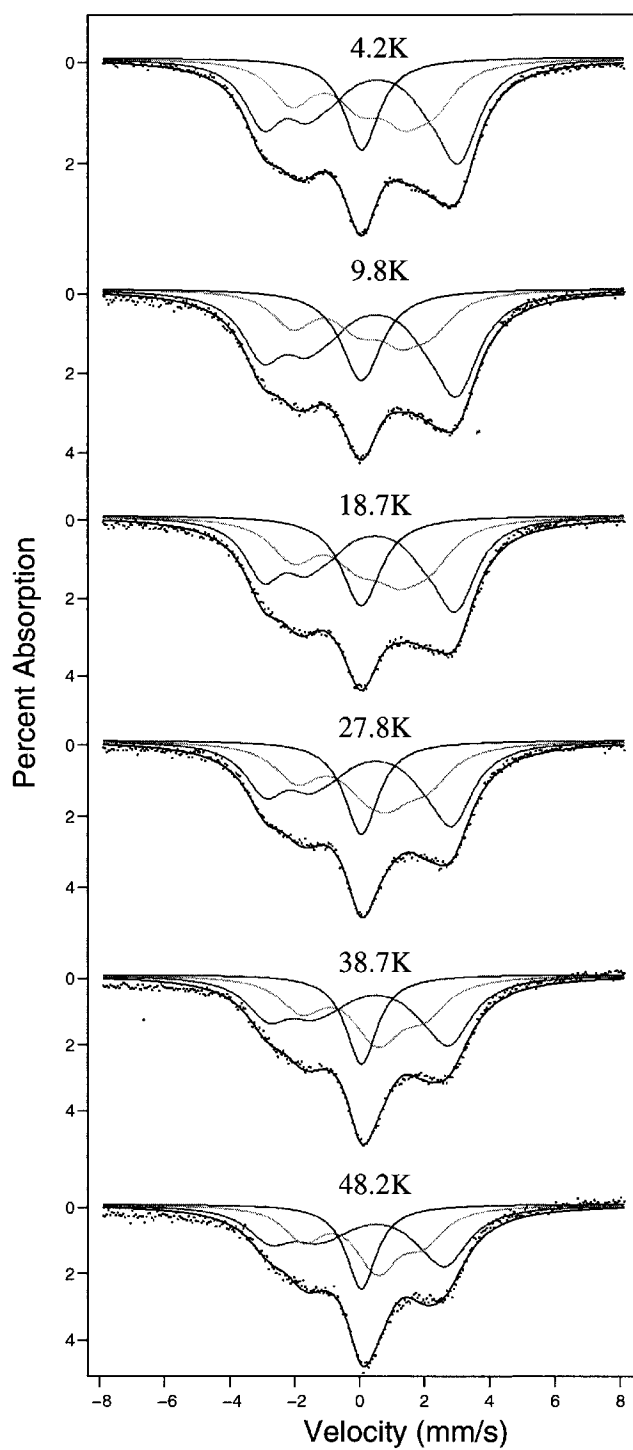


Figure 2. ^{119}Sn Mössbauer spectra in the temperature range 4.2–48.2 K. The spectra are fitted with three components, two for tin in different sites in $\text{RuSr}_2\text{GdCuO}_8$ and one for tin in the impurity SrSnO_3 phase.

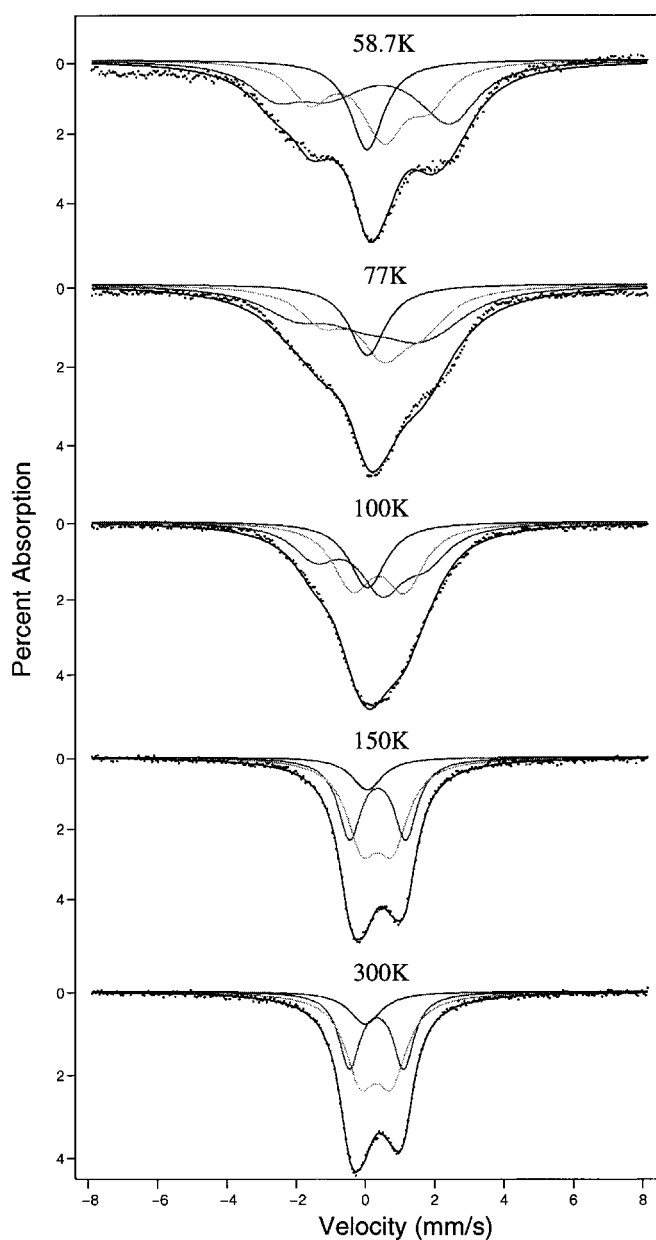


Figure 3. ^{119}Sn Mössbauer spectra in the temperature range 58.7–300 K. The spectra are fitted with the same components as in figure 2.

tin ion having one or more tin ions amongst its four nearest cation neighbours. Whilst both components 1 and 2 show a quadrupole shift consistent with the tetragonal site symmetry of the dopant tin ions, component 1 (the only strictly tetragonal site) is characterized by the smaller value. The isomer shift values for tin in both sites show that the tin ions are close to a Sn^{4+} configuration although the slightly larger values of isomer shift as compared to that of tin in SrSnO_3 (component 3) indicate a slightly larger electron density at the Sn^{4+} nucleus than in

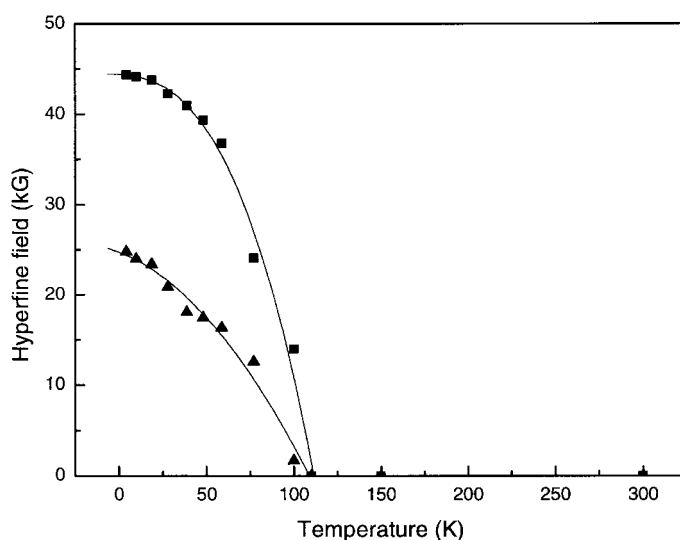


Figure 4. Variation of the hyperfine magnetic field on the tin sites in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ with temperature. The curves are seen to extrapolate to an ordering temperature of $T_c = 108 \pm 5$ K.

SrSnO_3 —indicative of a lower degree of ionicity. The fitting procedure gave area ratios of 44:37:19 for components 1, 2 and 3. This is in good agreement with the area ratios of 49:31:19 evaluated by assuming that 19% of the tin content is present in the SrSnO_3 impurity phase and assuming the random substitution of tin on the ruthenium site.

In the spirit of this model, and assuming that the f factors in SrSnO_3 and $\text{Ru}(\text{Sn})\text{Sr}_2\text{GdCu}_2\text{O}_8$ are similar, then the ratios of the areas of the components were kept approximately constant as the temperature of measurement was changed. The other parameters were allowed to vary as a function of temperature. The values of B_{hf} were zero at temperatures exceeding 100 K, i.e. above the ferromagnetic- to paramagnetic-phase transition temperature. The variation of hyperfine magnetic field, B_{hf} , with temperature for components 1 and 2 is shown in figure 4. Although the temperatures at which the spectra were recorded were not selected to enable an accurate determination of T_c , the results show that the values of both components extrapolate to a value for T_c of about 110 K. This is in good agreement with the bulk T_c recorded from samples of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ with similar levels of tin doping [12] and shows that the internal field is uniform over the two sites.

The accuracy of this model is tested by the quality of fits to the series of spectra shown in figures 2 and 3. The overall success of the fits attests to the appropriateness of the general picture although the difficulty in fitting the spectra at 77 and 100 K (where the Δ values are larger than in neighbouring spectra) indicates some local problems with some of the assumptions.

In fitting the ^{119}Sn Mössbauer spectra the angle θ between the direction of the hyperfine magnetic field and V_{zz} , the major axis of the electric field gradient, could be varied. It was found that good fits to all the magnetically split spectral components were achieved when $\theta \approx 0^\circ$, indicating that the hyperfine magnetic field is essentially parallel to the major axis of the electric field gradient. It is likely that V_{zz} lies along the four-fold rotation axis of the ruthenium sites, i.e. parallel to the crystallographic c axis. In this case the spectra indicate that the hyperfine magnetic field and the ruthenium magnetic moments also lie along the c axis, in agreement with neutron diffraction results [7]. The accuracy in determining θ from Mössbauer fits does not, however, distinguish between (i) the hyperfine field being directed along the local

(tilted) axis of the octahedron and (ii) being accurately directed along the crystal c axis. Thus we are not able to distinguish between a canted and a uniaxial spin system.

Acknowledgments

We thank EPSRC for the award of studentships (JB and ACM) and research grant GR/M599.76.

References

- [1] Fertig W A, Johnston D C, DeLong L E, McCallum R W and Maple M B 1977 *Phys. Rev. Lett.* **38** 987
- [2] Bauernfeind L, Widder W and Braun H F 1995 *Physica C* **254** 151
- [3] Tang K B, Qian Y T, Yang L, Zhao Y D and Zhang Y H 1997 *Physica C* **282–287** 947
- [4] Felner I, Asaf U, Reich S and Tsabba Y 1999 *Physica C* **311** 163
- [5] Bernhard C, Tallon J L, Niedermayer C, Blasius T, Golnik A, Brucher E, Kremer R K, Noakes D R, Stronach C E and Ansaldo E J 1999 *Phys. Rev. B* **59** 14099
- [6] McLaughlin A C, Zhou W, Attfield J P, Fitch A N and Tallon J L 1999 *Phys. Rev. B* **60** 7512
- [7] Lynn J W, Keimer B, Ulrich C, Bernhard C and Tallon J L 2000 *Phys. Rev. B* **61** 14964
- [8] McLaughlin A C, Attfield J P and Tallon J L 2000 *Int. J. Inorg. Mater.* **2** 95
- [9] Chmaisson O, Jorgensen J D, Shaked M, Dollar P and Tallon J C 2000 *Phys. Rev. B* **61** 6401
- [10] McLaughlin A C and Attfield J P 1999 *Phys. Rev. B* **60** 14605
- [11] McLaughlin A C, Janowitz V, McAllister J A and Attfield J P 2000 *Chem. Commun.* 1331
- [12] McLaughlin A C, Janowitz V, McAllister J A and Attfield J P 2000 *J. Mater. Chem.* **11** 173
- [13] Greenwood N N and Gibb T C 1971 *Mössbauer Spectroscopy* (London: Chapman and Hall) p 394