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InCuO_{2.5} and ScCuO_{2.5}: new oxidized copper delafossites with triangular lattices of Cu²⁺ cations

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Abstract

New oxidized delafossite compounds of composition InCuO_{2.5} and ScCuO_{2.5} are synthesized and their structures are characterized by means of x-ray and neutron powder diffraction. Oxygen intake is accompanied by a small increase of the unit cell, and a complex superstructure attributed to oxygen ordering appears. Average structure refinements show the presence of additional oxygen close to the centres of Cu triangles, and an average copper valence of +2. The two compounds appear to be isostructural. Magnetic measurements show a non-linear thermal increase of the inverse magnetic susceptibility up to some maximum, soon followed by a minimum around 280 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the field of research on frustrated magnetism, the search for new compounds which could provide tests for theoretical predictions or stimulate the development of more elaborate models is rapidly growing. Many compounds where magnetic frustration is based on the presence of antiferromagnetic interactions on a 3D pyrochlore-type lattice are now actively studied. The examples of 2D frustrated antiferromagnets, such as corner-sharing triangular lattices or Kagome arrays of spins, are encountered more seldom. In this respect, the oxidized copper delafossite compounds ACuO_{2+δ} are attractive materials for several reasons: they are based on simple structures, they display various types of planar triangular arrays of Cu²⁺ spin 1/2 cations, and these arrays can be doped by changing the oxygen content.

The delafossite structure A³⁺B⁺O₂ can be described as the alternate stacking of AO₂ layers of edge-sharing AO₆ octahedra and planes of B⁺ cations arranged as a planar triangular network. The B⁺ cations have a dumb-bell coordination with two oxygen anions from the planes above and below. Depending on the manner of stacking of the AO₂ and B layers, structural variants with hexagonal (called 2H, space group *P6₃/mmc*) or rhombohedral (called 3R, space group *R $\bar{3}m$*) symmetry can be formed. The absence of interatomic bonds in the B cation planes gives a

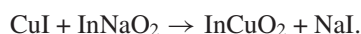
great flexibility to this structure, in which a large number of A^{3+} cations can be accommodated, with radii ranging from 0.54 Å (for Al^{3+}) to 1.16 Å for (La^{3+}). Ten years ago, Cava *et al* [1] showed that for large A^{3+} cations such as La^{3+} or Y^{3+} , additional oxygen can be inserted into the structure of $ACuO_2$ compounds up to oxygen contents δ as large as 0.5 or even 0.67. The copper cation valence becomes +2 for $\delta = 0.5$ and +2.33 for $\delta = 0.67$. Thus, one can expect the formation of triangular arrays of spin 1/2 Cu^{2+} cations for $\delta = 0.5$, which could then be hole doped for higher δ values. Preliminary studies were limited by sample quality due to intergrowth of 2H and 3R variants, and/or to oxygen disorder. More recently, by optimizing the synthesis procedure, we were able to obtain the crystal structures of $YCuO_{2.5}$ [2] and $LaCuO_{2.66}$ [3], and a detailed study of the physical properties of these compounds is now under way [4]. For example, $YCuO_{2.5}$ is obtained by oxidation of 2H- $YCuO_2$. The oxygen intake is accompanied by a change of symmetry from hexagonal ($P6_3/mmc$, $a_{2H} = 3.52$ Å, $c_{2H} = 11.42$ Å) to orthorhombic ($Pnma$, $a_0 = 6.20$ Å $\approx a_{2H}\sqrt{3}$, $b_0 = 11.22$ Å $\approx c_{2H}$ and $c_0 = 7.15$ Å $\approx 2b_{2H}$). The additional oxygen anions are inserted at the centres of copper cation triangles, and ordered in such a way as to form undulating chains of triangles sharing corners in the a -axis direction.

These previous studies have shown that the type of oxygen ordering and copper cation arrangement may depend on the oxygen content as well as on the nature of the A^{3+} cation. Therefore, it was interesting to study the effects of oxygen insertion in other copper delafossites. Here we report on the synthesis and characterization of two such new compounds: $InCuO_{2.5}$ and $ScCuO_{2.5}$.

2. Sample preparation

2.1. $InCuO_{2.5}$

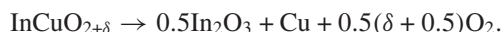
In order to synthesize oxidized delafossites, the $ACuO_2$ compound must first be prepared, and then treated in an oxidizing atmosphere. The first attempts to prepare $InCuO_2$, carried out by using solid state reaction between In_2O_3 and Cu_2O under reducing conditions, were unsuccessful, as previously reported by Hahn and Lorent [5]. Another route through the synthesis of an $In_2Cu_2O_5$ precursor was also tried. The precursor was prepared by reacting a stoichiometric mixture of In_2O_3 and CuO at 1050 °C in air for 24 h. High temperature treatment in nitrogen atmosphere led to complete decomposition of the precursor into In_2O_3 and Cu_2O , without formation of the $InCuO_2$ delafossite phase. Then, we tried the cation exchange reaction as previously described for the synthesis of $InAgO_2$ [6] and $ScCuO_2$ [7]. In this case, the $InNaO_2$ compound (α - FeO_2 structure) is reacting with CuI following the equation



$InNaO_2$ was first prepared by solid state reaction of an In_2O_3 and Na_2CO_3 mixture with 10% excess of Na_2CO_3 at 900 °C for 20 h under oxygen flow. The $InNaO_2$ powder obtained was found to be single phase by means of x-ray powder diffraction. It was mixed with CuI in a 1:1 Cu to Na molar ratio and pressed into bars of size 0.5 cm \times 0.5 cm \times 3 cm. These bars were placed into vacuum-sealed quartz tubes and heated at various temperatures for two days. The reaction products were treated in an aqueous ammoniac solution to dissolve the NaI , and dried at 100 °C. The resulting samples were analysed by means of x-ray powder diffraction. The exchange reaction is shown to occur above 400 °C, below which the starting mixture is found to be unchanged. Above 500 °C, In_2O_3 and Cu_2O are obtained. Between 400 and 500 °C, a new phase is formed, and the powder diffractogram can be completely indexed by using a rhombohedral unit cell with $a = 3.28$ Å and $c = 17.36$ Å, typical of a 3R-type delafossite

structure. During the course of this work, Shimode *et al* [8] reported the preparation of InCuO₂ by a similar exchange reaction using CuCl and LiInO₂.

The oxygen intake was studied by thermogravimetric analysis under oxygen at a 2 °C h⁻¹ heating rate. Above 200 °C, a regular mass increase indicates the beginning of oxidation, up to a plateau corresponding to the O_{2.5} stoichiometry, starting close to 500 °C. Above 550 °C, a slight anomaly in the TGA curve indicates the transformation of InCuO_{2.5} into the In₂Cu₂O₅ phase, as shown by *ex situ* x-ray analysis. Based on these observations, InCuO_{2.5} was prepared by heat treatment of InCuO₂ at 450 °C for one day under oxygen flow. The oxygen content of the resulting sample was determined to be 2.50(3) by TGA analysis of the decomposition reaction in Ar atmosphere:



2.2. ScCuO_{2.5}

Similarly to what we had reported for YCuO₂, the possible existence of the two structural variants 2H and 3R complicates the preparation of ScCuO₂. Attempts to use solid state reaction technique conditions determined for YCuO₂ [2] failed to lead to a single phase of either compound. Here also, we had to use a cation exchange reaction, as previously reported by Doumerc *et al* [7], following the equation



ScNaO₂ was prepared by solid state reaction of a Sc₂O₃ and Na₂CO₃ mixture heated at 950 °C for 20 h under oxygen flow. The exchange reaction was carried out as described above for InCuO₂. A 3R delafossite-type phase ($a = 3.21$ Å, $c = 17.08$ Å) containing Sc₂O₃ as an impurity was obtained at a 550 °C reaction temperature. TGA analysis under oxygen shows oxygen intake behaviour similar to that found for InCuO₂. In order to prepare ScCuO_{2.5}, oxygen treatments were carried out at 500 °C, with several intermediate regrindings. Analysis of the oxygen content of the final product by reductive decomposition in Ar atmosphere indicated a 2.43(3) oxygen stoichiometry.

3. Structural characterization

The four samples obtained (InCuO₂, ScCuO₂, InCuO_{2.5}, and ScCuO_{2.5}) were characterized by means of x-ray powder diffraction using a Bruker D8 diffractometer in Bragg–Brentano geometry, equipped with a focusing primary Ge(111) monochromator and a Moxtek solid state detector. Neutron powder diffraction spectra have been collected on the D1B instrument of the ILL with a 1.28 Å wavelength between 10° and 90° two-theta. High resolution neutron powder diffractograms of the oxidized samples were recorded on the D1A instrument of the ILL, with a 1.91 Å wavelength obtained by using the (511) reflection of a Ge monochromator, between 10° and 145° two-theta with a 0.05° step size. All data were analysed by the Rietveld technique using the WinPlotr/Fullprof software [9]. The refined parameters, interatomic distances, and cation valences (calculated by the bond valence sum technique [10] with FullProf) are shown in table 1.

The structures of InCuO₂ and ScCuO₂ are typical of the 3R delafossite type, with In (respectively Sc) on the 3*b* (0 0 1/2) position, Cu at the 3*a* (0 0 0) position and O at the 6*c* (0 0 *z*) position, with *z* close to 0.11. For the oxidized samples, the x-ray diffractograms do not reveal a large modification with respect to the parent delafossite compounds. Most reflections can still be indexed on the basis of the 3R-type unit cell, with an increase of *a*

Table 1. Structural data obtained by means of neutron powder diffraction on D1A (InCuO_{2.5} and ScCuO_{2.5}) and D1B (InCuO₂), and x-ray powder diffraction (ScCuO₂). All refinements are carried out in the $R\bar{3}m$ space group.

	InCuO ₂	InCuO _{2.5}	ScCuO ₂	ScCuO _{2.5}
<i>a</i>	3.3042(2)	3.3205(1)	3.2164(1)	3.2673(1)
<i>c</i>	17.453(8)	17.3549(9)	17.0904(3)	17.0308(9)
<i>V</i>	165.02	165.72	153.12	157.45
<i>B</i> (In/Sc)	0.13(7)	2.3(1)	0.55(5)	2.41(6)
<i>B</i> (Cu)	0.70(6)	1.64(6)	1.07(5)	0.93(6)
<i>z</i> (O1)	0.1055(1)	0.1076(1)	0.1103(3)	0.1095(2)
<i>B</i> (O1)	0.34(5)	1.23(5)	−0.2(1)	1.01(6)
<i>z</i> (O2)		0.0156(4)		0.0177(6)
<i>n</i> (O2)		0.66(1)		0.61(1)
<i>B</i> (O2)		2.5(3)		2.4(4)
<i>d</i> (In/Sc–O1)	2.186(1)	2.174(1)	2.092(2)	2.123(1)
<i>d</i> (In/Sc–O2)		2.622(7)		2.538(9)
<i>V</i> (In/Sc)	2.784(3)	2.968(3)	3.114(8)	2.958(5)
<i>d</i> (Cu–O1)	1.841(2)	1.867(2)	1.886(5)	1.865(3)
<i>d</i> (Cu–O2)		1.936(1)		1.910(2)
<i>V</i> (Cu)	1.0223(4)	2.189(5)	0.907(9)	2.185(7)
<i>R</i> _{wp}	8.28	11.5	16.6	9.07
<i>R</i> _{Bragg}	2.94	11.1	6.65	9.01

and decrease of *c* parameters, leading to a global increase of the cell volume. Only a few extremely weak peaks cannot be indexed using this unit cell. More of these can be detected in the high resolution neutron powder diffraction spectra collected on D1A. Preliminary electron diffraction data obtained on InCuO_{2.5} [11] indicate the existence of a complex superstructure with a unit cell which was too large to allow a reliable structural determination until now. Similar superstructure reflections are visible in the D1A data for both oxidized compounds, which indicates that they are probably isostructural. Further investigations are under way to obtain the full structure.

Therefore, we were limited to refinements in the average delafossite structure. After convergence, a Fourier difference calculation indicated the presence of peaks at the (1/3 2/3 0) and (2/3 1/3 0) positions, which were attributed to the additional oxygen atoms. Refinements were continued by adding oxygen in these positions, and refining the occupancy and isotropic displacement parameter. Further improvement was obtained by placing oxygen O2 at 6c (1/3 2/3 *z*) with *z* close to 0 and refining the *z* value. The refined *z* values correspond to a shift from the *z* = 0 plane by about 0.3 Å. The refined occupancies are higher than expected from the TGA data given above, but the large displacement parameters and the shift from the Cu planes indicate that the refined O2 position corresponds to the average of different local sites, the ordering of which is most probably responsible for the superstructure. It is not surprising that one obtains unreliable occupancy values in these circumstances. Nevertheless, it is quite clear that oxygen is incorporated in the structure close to the centres of the copper triangles. The BVS calculation based on these data indicates average valences close to 2+ for the Cu cations, as expected from a 2.5 oxygen content. It is interesting to note that the structure of this two new compounds is different from that of YCuO_{2.5}, and may provide another example of a triangular arrangement of spin 1/2 Cu²⁺ cations. The refinement quality can be seen in figure 1 for InCuO_{2.5}.

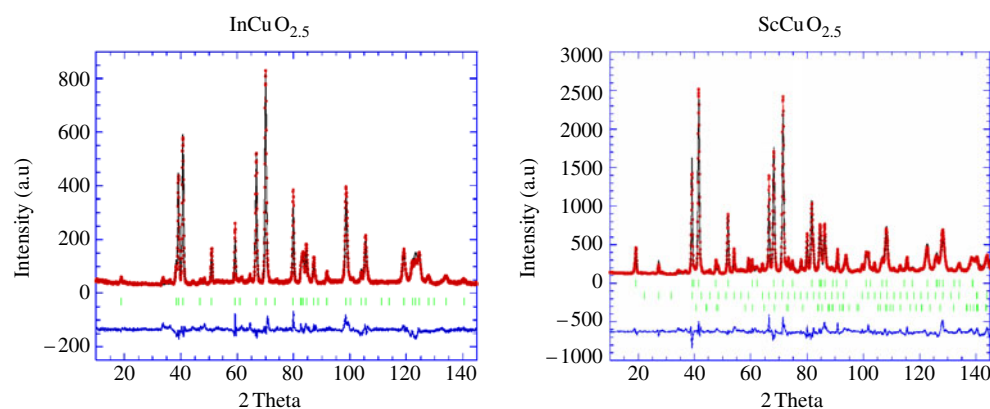


Figure 1. Rietveld refinement results for InCuO_{2.5} (left) and ScCuO_{2.5} (right). For the latter, the impurity phases are Sc₂O₃ and CuO.

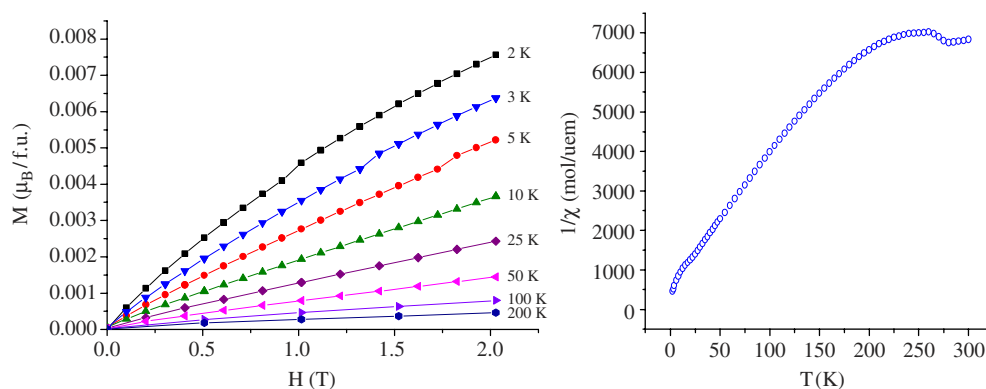


Figure 2. $M(H)$ isotherms and the inverse susceptibility versus T curve for InCuO_{2.5}.

4. Magnetic measurements

The magnetization versus field curves for InCuO_{2.5} were recorded between 0 and 2 T as a function of the temperature in the 2–300 K range on a vibrating sample magnetometer, and the magnetic susceptibility (figure 2) was deduced from Arrot–Belov plots when the magnetic isotherms were non-linear, below 20 K, and by a straight line extrapolation to zero magnetism when the magnetic isotherms were linear, above 20 K.

The deduced magnetic susceptibility is unusual. The inverse susceptibility increases with increasing temperature faster up to 20 K, quasi-linearly between 20 and 120 K, and then non-linearly up to a maximum at 250 K. An angular minimum is observed at 280 K, which could indicate some freezing. Magnetization measurements performed on a SQUID magnetometer confirm this behaviour, and show no difference between the FC (10 mT) and ZFC curves.

A quite similar behaviour was found for ScCuO_{2.5}, as shown by the inverse susceptibility versus T curve of figure 3. The maximum now at 225 K is better defined.

The complex magnetic behaviour shown by these two compounds is hard to interpret in the absence of more detailed structural information. It is interesting to note that neutron powder diffraction data collected at 2 K on the D1B instrument for InCuO_{2.5} do not show

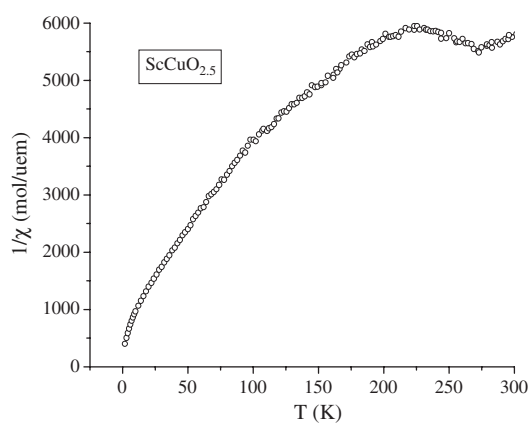


Figure 3. The inverse susceptibility versus T curve for $\text{ScCuO}_{2.5}$.

any meaningful modification with respect to the room temperature data, which indicates the absence of long range magnetic order at this temperature.

Acknowledgment

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References

- [1] Cava R J *et al* 1993 *J. Solid State Chem.* **104** 437
- [2] Van Tendeloo G *et al* 2001 *J. Solid State Chem.* **156** 428
- [3] Garlea O *et al* 2003 *Solid State Sci.* **5** 1095
- [4] Simonet V *et al* 2003 *J. Phys.: Condens. Matter*
- [5] Hahn H and Lorent C 1955 *Z. Anorg. Allg. Chem.* **279** 281
- [6] Shannon R D, Rogers D B and Prewitt C T 1971 *Inorg. Chem.* **10** 713
- [7] Doumerc J-P, Ammar A and Wichainchai A 1987 *J. Phys. Chem. Solids* **48** 37
- [8] Shimode M *et al* 2000 *J. Solid State Chem.* **151** 16
- [9] Rodríguez-Carvajal J and Roisnel T 1998 *FullProf.98 and WinPLOTR: New Windows 95/NT Applications for Diffraction* Newsletter No 20 Commission For Powder Diffraction, International Union for Crystallography
- [10] Brese N E and O'Keeffe M 1991 *Acta Crystallogr. B* **47** 192
- [11] Van Tendeloo G, unpublished results