Exploring the Structural and Magnetic Phase Transition of Cu$_{1-x}$Co$_x$Sb$_2$O$_6$

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The system Cu$_{1-x}$Co$_x$Sb$_2$O$_6$ has been investigated using sealed-tube and synchrotron X-ray powder diffraction, neutron powder diffraction and single crystal neutron diffraction. An orthorhombic phase is proposed between the previously established tetragonal and monoclinic phases for x < 1. In addition, evidence is presented for a possible ferroelastic phase transition in Cu$_{0.3}$Co$_{0.7}$Sb$_2$O$_6$ single crystals at low temperatures. Magnetic susceptibility measurements confirm antiferromagnetic ordering across the complete solid solution series.

1. Introduction

CuSb$_2$O$_6$ has been the most intensively studied compound in the ternary Cu-Sb-O system since the high transition temperature ($T_c$) superconducting materials based on copper oxides were found by Bednorz and Müller in 1986 [1]. It is reported to undergo a second-order phase transition from a tetragonal to a monoclinic distorted trirutile structure between 100 and 130 °C [2]. The transition is thought to be driven by a Jahn-Teller distortion on Cu$^{2+}$ (a d$^9$ ion, stabilising square-planar geometry). This square lattice cupric oxide layer is similar to that found in the two-dimensional Heisenberg antiferromagnet (HAF) La$_2$CuO$_4$, [3, 4]; however, the magnetic behaviour of CuSb$_2$O$_6$ is considered to be an S=$\frac{1}{2}$ one-dimensional Heisenberg antiferromagnet with strong anisotropy above 20 K [2]. The difference between these two compounds can be understood by applying and combining the total energy and tight-binding model calculation results [5]. A sudden decrease in magnetic susceptibility at 8.6 K indicates antiferromagnetic long-range ordering due to inter-chain interactions [2], and has recently been revealed as a crossover behavior from S = $\frac{1}{2}$ one-dimensional HAF to a three-dimensional HAF [8]. CuSb$_2$O$_6$ also exhibits a spin-flop transition at 2.2 T and 5 K, leading to greatly enhanced magnetic moments [6].

CoSb$_2$O$_6$ also crystallizes in the tetragonal trirutile structure (Fig. 1) and exhibits two-dimensional HAF behaviour with a broad transition at about 35 K [7]. The magnetic structure of CoSb$_2$O$_6$ has only been refined against neutron powder diffraction (NPD) data. Two alternative models for antiferromagnetic ordering have been proposed, which are indistinguishable by NPD [7].

This study concerns the doping of divalent Co onto the A site of CuSb$_2$O$_6$, which is of interest for two reasons. Firstly, a direct second-order phase transition from a tetragonal to a monoclinic trirutile ought not to be possible. A systematic reduction in symmetry, as shown in Bärnighausen trees, would require the existence of an orthorhombic...
intermediate phase. Secondly, this doping changes the magnetic behaviour from a $S=\frac{1}{2}$ one-dimensional Heisenberg antiferromagnet to a two-dimensional Heisenberg antiferromagnet. The main aim of this study is thus to investigate the structural and magnetic behaviour of the solid solutions $(\text{Cu}_{1-x}\text{Co}_x)\text{Sb}_2\text{O}_6$ in combination with very detailed investigations of the phase transition of $\text{CuSb}_2\text{O}_6$.

2. Sample preparation

Stoichiometric mixtures of $\text{CuO}$, $\text{Co}_3\text{O}_4$ and $\text{Sb}_2\text{O}_3$ powders were placed in corundum crucibles and heated to 960 °C for 36-48 hours in a muffle furnace prior to quenching in air yielding in phase pure powders. Powder samples were initially characterized by X-ray powder diffraction (XRD) using a sealed-tube source (Panalytical Empyrean, monochromated Cu K$_\alpha$ radiation, 10 - 80° 20 range). Synchrotron X-ray powder diffraction (SXRD) data were subsequently collected on the Powder Diffraction beamline (10-BM) at the Australian Synchrotron over a 6 to 86° 20 range with a step size of 0.00375° 20, using the MYTHEN detector and the double crystal monochromator of Si(111) flat crystal pair ($\lambda = 0.774235$ Å, calibrated with LaB$_6$). Single crystal neutron Laue diffraction data were collected on the instrument Koala at the OPAL research reactor, Lucas Heights, Australia. Complete single crystal data sets were collected at 100 K, 25 K and 5 K (well above, close to, and below the magnetic ordering temperature respectively) for each crystal, comprised of 0.5 h measurements taken at 15 different orientations. Magnetic susceptibility data from room temperature to 2 K were collected on a Quantum Design Physical Properties Measurement System (PPMS) in zero-field-cooled mode using a 1 T magnetic field.

3. Results

3.1 X-ray Powder Diffraction Analysis

Sealed-tube XRD data were collected from samples prepared at 960 °C and quenched in water. Preparations using slower cooling rates from high temperatures down to room temperature could not preserve the 960 °C structure, the sample composition was identical in all cases independent of cooling rate. At room temperature, a wide two-phase region was observed from $x = 0.2$–0.5, involving a Cu-rich monoclinic phase and a Co-rich tetragonal phase. For the monoclinic Cu-rich component, all the lattice constants increase from $x = 0$–0.15 (Fig. 2). Between 0.2 and 0.5, the lattice constants $a$ and $b$ are relatively constant, while $c$ decreases slightly. The tetragonal phase could be Rietveld-refined starting from $x = 0.2$, with the lattice constant $a$ increasing and $c$ decreasing from $x = 0.2$–1. Despite the observed doping trend and two-phase region, it was not possible to fully interpret the phase behaviour of the system based on these XRD data, due to difficulties in refining two phases distinguished only by a small monoclinic distortion (~1°).

Fig. 2. Lab X-ray powder diffraction patterns of $(\text{Cu}_{1-x}\text{Co}_x)\text{Sb}_2\text{O}_6$ solid solutions (left) and lattice constants distribution of $(\text{Cu}_{1-x}\text{Co}_x)\text{Sb}_2\text{O}_6$ solid solutions (right).
3.2 High Resolution Synchrotron Powder Diffraction Analysis

SXRD data were used to analyse the two-phase region in more detail. These data confirmed the existence of a two-phase region at room temperature. At 200 °C, we had expected to observe a complete solid-solution in the tetragonal phase, as the tetragonal-monoclinic phase transition of CuSb$_2$O$_6$ is observed around 100 °C to 130 °C; however, the SXRD data indicate that this is not the case (Fig. 3). An orthorhombic phase is clearly identifiable on the Cu-rich side, including undoped CuSb$_2$O$_6$. The proposed space group is $Pnmm$, which is the only possible space group according to Bärnighausen trees. A second order transition from the tetragonal modification ($P4_2/mnm$) to the monoclinic modification ($P2_1/n$) can be related via translationsgleiche group-subgroup relations but only via an orthorhombic modification ($Pnnm$):

$$P4_2/mnm \rightarrow Pnmm \rightarrow P2_1/n$$

The structural distortion in $Pnmm$ is very subtle, even using synchrotron radiation. Nevertheless, the diffraction peaks clearly show different behaviours on the Cu-rich and the Co-rich sides of the solid solution, indicating the presence of two different structural modifications (Fig. 3). No additional peaks were observed that could indicate a superstructure ordering of Cu and Co. The orthorhombic phase was observed at 200 °C for the entire Cu$_{1-x}$Co$_x$Sb$_2$O$_6$ solid solution except CoSb$_2$O$_6$.

Even at 500 °C, we still observe different symmetries on the Cu-rich and Co-rich ends of the solid solution. The phase transition from tetragonal to lower symmetry can be observed for compositions of $x = 0$–0.3 (Fig. 3). All these transitions were fully reversible.

Fig. 3. SXRD patterns of Cu$_{1-x}$Co$_x$Sb$_2$O$_6$ solid solutions at 200 °C (left) and Rietveld refinement of synchrotron powder diffraction data of Cu$_{0.3}$Co$_{0.7}$Sb$_2$O$_6$ at 500 °C (right).

3.3 Single Crystal Neutron Laue Diffraction

Single crystal Laue diffraction data were collected for CuSb$_2$O$_6$, Cu$_{0.3}$Co$_{0.7}$Sb$_2$O$_6$ and CoSb$_2$O$_6$ single crystals. The trirutile structure of CoSb$_2$O$_6$, which could be refined against these data, is shown in Fig. 1. All CuSb$_2$O$_6$ crystals were twinned and could not refined successfully. For Cu$_{0.3}$Co$_{0.7}$Sb$_2$O$_6$, after the initial appearance of diffuse scattering below room temperature, a peak splitting could be observed on decreasing the temperature from to 100 K and then 5 K (Fig. 4). This peak splitting was reversible on increasing the temperature, which suggests a ferroelastic phase transition.
3.4 Magnetic Measurements

The magnetic susceptibility behaviour of Cu$_{1-x}$Co$_x$Sb$_2$O$_6$ from x = 0.3 and 0.7 is similar to that of CoSb$_2$O$_6$ (Fig. 5), confirming antiferromagnetic ordering across the entire solid solution. The transition is broad, as reported for the pure Co sample (x = 1) [7]. The composition at x = 0.1 shows behaviour more akin to that of the pure Cu sample (x = 0). The change in Néel temperatures is small for x = 0–0.7 (13 K difference) but a significant jump is observed to x = 1 CoSb$_2$O$_6$ (13 K difference, Fig. 5 inset). It appears that all these compounds except the Cu-rich samples are likely to exhibit 2D HAF behavior, with magnetic susceptibility decreasing in accordance with the reduced moment of Cu(II) compared to Co(II).

Fig. 5. Magnetic susceptibility data (x = 0, 0.1, 0.3, 0.7 and 1, from the bottom to top) and Néel temperatures for Cu$_{1-x}$Co$_x$Sb$_2$O$_6$.

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References