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# BRIEF COMMUNICATION

# Confirmation of Long-Range Magnetic Order in $CuSb_2O_6$

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**The presence of long-range order in $CuSb_2O_6$ was confirmed by low-temperature neutron diffraction data. A magnetic superlattice reflection was indexed with the wavevector $k = (\frac{1}{2}, 0, \frac{1}{2})$. This propagation vector is identical to that of $CoSb_2O_6$. The extremely weak intensity of the magnetic reflection prevented the analysis of the neutron data by Rietveld refinement, but instead the magnetic moment was obtained by simulating the diffraction pattern while varying the magnetic moment of $Cu^{2+}$. A moment value of 0.5 $\mu_B$ is believed to be the best approximation for the actual moment at 5 K. Further evidence for the presence of the ordered state is obtained from a spin–flop phase transition which occurred at 2.2 T at 5 K in a single crystal.** 

## INTRODUCTION

Previously, we reported the refinement of the crystal structure and studied the magnetic susceptibility behavior of $CuSb_2O_6$ (1). This material was found to adopt a monoclinically distorted trirutile structure and it crystallizes in the space group $P2_1/n$. Atomic positions were determined by profile refinement of neutron powder diffraction data in the unit cell, $a = 4.6349(1)$Å, $b = 4.6360(1)$Å, $c = 9.2931(1)$Å, $\beta = 91.124(2)°$. Magnetic susceptibility data exhibit a broad maximum at about 60 K and an abrupt transition at 8.5 K. The high-temperature data can be fitted to a Curie–Weiss law giving $\mu_{eff} = 1.758\ \mu_B$ and a Weiss constant, $\theta$, of −48 K. Although the crystal structure indicates a nearly square planar $Cu^{2+}$ lattice as in other trirutiles, a Cu–O–O–Cu superexchange pathway seems to be dominant, giving rise to short-range correlations which are approximately one-dimensional. The high-temperature susceptibility is fitted well to the predictions of the one-dimensional Heisenberg model with $J/k = -46.9$ K.

One-dimensional systems cannot undergo a phase transition to a long-range ordered state at any finite temperature. As all magnetic compounds exist in three space dimensions, interplanar exchange and out-of-plane forces will act to induce long-range magnetic ordering at temperatures higher than 0 K (2). It is not yet clear how the long-range ordered state evolves from the short-range ordered (SRO) regime in the trirutile oxides. Following Ref. (2) there are three relevant exchange pathways to consider: $J_1$, involving linear $M$–O–O–$M$ along ⟨110⟩, and $J_2$, involving bent $M$–O–$M$ along ⟨$\bar{1}$10⟩, both of which are intraplanar, and $J_3$, which is interplanar. Furthermore, intraplanar interchain coupling is geometrically frustrated as is the interplanar coupling due to the body-centered tetragonal magnetic sublattice. Possible situations include $J_1 \approx J_2$, giving rise to two-dimensional SRO, which may or may not (in the case of Ising spins) require a finite $J_3$ for LRO. In contrast, if $J_1 \gg J_2$, LRO could still be realized by interplanar coupling of the ⟨110⟩ chains following the analysis of Villain and Loveluck (3).

For $CoSb_2O_6$ there is some evidence for the former scenario as the critical exponent, $\beta$, measured down to a reduced temperature $t = [T_c - T]/T_c$ of $9 \times 10^{-4}$, is consistent with the two-dimensional Ising model. The case of $CuSb_2O_6$ may in contrast represent the latter scenario, given the strong indication that $J_1 \gg J_2$. Thus, the abrupt decrease in the susceptibility at 8.5 K could signal the crossover from one-dimensional to three-dimensional LRO. There is an additional, not impossible, origin for this 8.5-K feature which is a spin–Peierls transition, such as that recently reported for $CuGeO_3$, which contains similar linear Cu–O–O–Cu linkages (4). Thus, neutron diffraction and single crystal magnetization measurements were carried out in an effort to clarify the situation.

Preliminary data sets were taken at 4.2 K at the McMaster Nuclear Reactor (MNR). There was no definitive sign of any magnetic superlattice reflections in the data collected at MNR, indicating that the copper magnetic moment may be much less than 1 $\mu_B$. In this Communication, we report the results of low-temperature neutron diffraction on the Dualspec diffractometer at Chalk River

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Nuclear Laboratory, where the neutron flux is much higher.

## EXPERIMENTAL

Low-temperature neutron data were collected on Dualspec at the Chalk River Nuclear Laboratory using 1.4999-Å neutrons. Data sets were collected at temperatures of 5 and 12 K. The superlattice reflection was fitted to a Gaussian peakshape to determine its $2\theta$ angle. The magnetic pattern simulation was calculated using the RIETAN program written by Izumi (5). The magnetic form factor for $Cu^{2+}$ was obtained from Brown (6).

Single crystals were grown from a $V_2O_5$ flux (7), which will be described in detail elsewhere. A single crystal with the dimensions 2 × 2 × 0.5 mm was mounted on a goniometer head and oriented in such a way that the direction of the field in the SQUID magnetometer is parallel to the easy axis of the crystal. The sample was cooled in the SQUID to 5 K and the magnetic moment was measured as a function of the field at this temperature.

## RESULTS AND DISCUSSION

A very weak superlattice reflection was observed at 5 K and vanished at 12 K in the data from the Dualspec diffractometer, as shown in Fig. 1. After correcting for the zero angle shift, the peak position was found to be 8.1°. This peak was indexed as $(\frac{1}{2}, 0, \frac{1}{2})$ on the chemical cell which led to the assignment of the propagation vector $k = (\frac{1}{2}, 0, \frac{1}{2})$ for the ordered state. This proposition is in line with those reported for other trirutile oxides. In these oxides, there are basically two magnetic structures reported: the most commonly occurring magnetic structure is described by propagation vector $k = (\frac{1}{2}, 0, \frac{1}{2})$, which is adopted by the oxides $CoSb_2O_6$ (8), $NiSb_2O_6$ (9), and $FeTa_2O_6$ (10), and the other known propagation vector is $k = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, which is reported in the case of the oxides $CoTa_2O_6$ and $NiTa_2O_6$ (8, 11). Despite the similarity between the trirutile structure and that of $K_2NiF_4$, the magnetic structures in the trirutile oxides are larger and more complex than those found for $K_2NiF_4$ compounds. It has been argued that this is a direct result of the competition between the interplanar and intraplanar interactions (2). The less favorable superexchange pathways in the trirutiles give rise to much smaller intraplanar exchange constants than in $K_2NiF_4$ compounds and to a dominant next-nearest neighbor interaction. Further, there are two inequivalent second neighbor interactions and competition between these and the first neighbor interaction gives rise to complex magnetic behavior.

For the propagation vector $k = (\frac{1}{2}, 0, \frac{1}{2})$ two magnetic structures are equally consistent with the powder data. The magnetic structures can be described in terms of two sublattices (origin and body-center) where the moments within one sublattice are antiparallel along ⟨100⟩ and ⟨001⟩ but parallel along ⟨010⟩. All moments lie within the *ab* plane along ⟨110⟩ and ⟨1$\bar{1}$0⟩. The structures differ in the angle of the moments between the two sublattices. Schematic illustrations of the magnetic unit cell are shown in Fig. 2; the collinear model is shown on the left and the orthogonal model on the right.

Because of the weak intensity of the magnetic reflection in $CuSb_2O_6$, it was not possible to refine the magnetic structure using Rietveld refinement. Instead, a simulation of the intensity of the peaks was attempted where the magnetic moment was varied between 0.5 and 1.0 $\mu_B$.

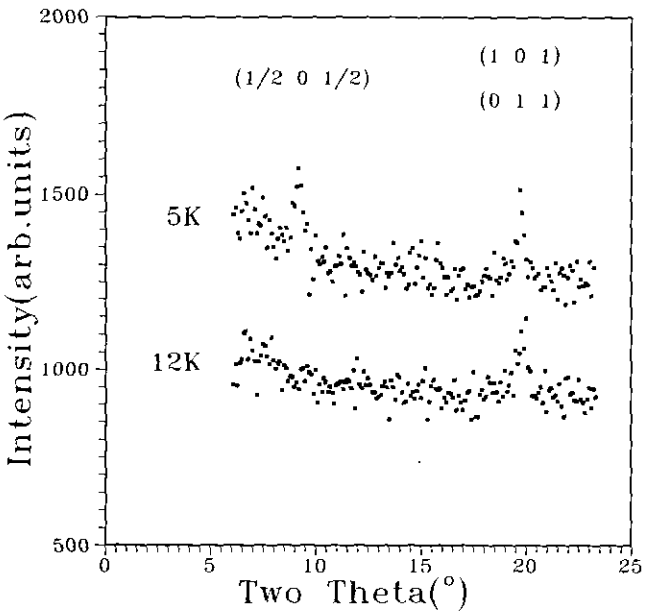


FIG. 1. Low-temperature neutron scattering patterns for $CuSb_2O_6$ at 5 and 12 K.

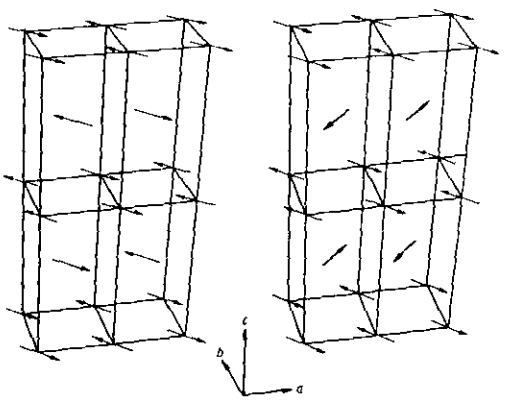


FIG. 2. Schematic illustrations of the $(2a, a, 2c)$ magnetic cell of $CuSb_2O_6$. The collinear model is on the left and the orthogonal model is on the right.

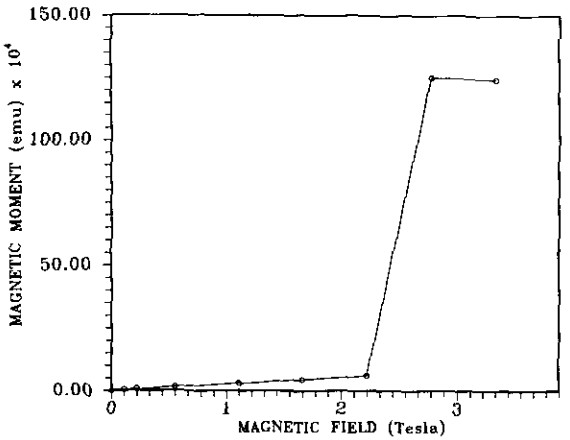


FIG. 3. Magnetization versus magnetic field for a $CuSb_2O_6$ single crystal at 5 K.

This simulation was carried out using the RIETAN program. After careful assessment of the simulated patterns, it was found that an upper limit for the magnetic moment is 0.5(1) $\mu_B$, because for moment values as large as 0.7 $\mu_B$, another magnetic reflection at 15.48° with the Miller indices $(\frac{1}{2}, 0, \frac{3}{2})$ appears which vanishes when the moment was set at 0.5 $\mu_B$. Simulations with a moment value as large as 1.0 $\mu_B$, which would be consistent with the observed moment in the paramagnetic regime, are completely unreasonable. A similar result was reported for $La_{2-x}Sr_xCuO_4$ (12) in which the magnetic moment of $Cu^{2+}$ was as low as 0.5 $\mu_B$. This may be due to the fact that superexchange interactions partly delocalize the unpaired spin or may be due to the frustration, which can also lead to low moments.

Further evidence for the presence of long-range order could be drawn from the spin–flop phase transition. This was observed for the $CuSb_2O_6$ single crystal, as is evident in the behavior of the magnetization as a function of the magnetic field, plotted in Fig. 3, which shows clearly the presence of the spin–flop transition at 2.2 T at 5 K.

Based on these findings, one can conclude with certainty the claim made previously (1) about the presence of an ordered state in this material, although the ordered moment on $Cu^{2+}$ is anomalously small.

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