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BRIEF COMMUNICATION

On $CuCrP_2S_6$: Copper Disorder, Stacking Distortions, and Magnetic Ordering

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The pseudo-one-particle potential for Cu^I in $CuCrP_2S_6$ was calculated from the room temperature (RT) structural model and shown to have a double-well shape straddling the center of the CuS_6 octahedron. It is argued that this finding supports the thermal hopping interpretation of the RT copper disorder in this compound. The RT monoclinic unit cell parameters were also remeasured and found to be consistent with the presence of out-of-plane packing deformations. Last, the antiferromagnetic structure of the Cr^{III} moments below $T_N \approx 30$ K was determined using neutron powder diffraction. © 1995 Academic Press, Inc.

The room temperature (RT) structure and magnetic study of $CuCrP_2S_6$ published by Colombet *et al.* (1) gave the first example of an unusually extended electronic density associated with the monovalent cation in a lamellar $M^IM'^{III}P_2S_6$ phase (M = Ag, Cu, and M' = V, Cr, In, Sc) (2, 3) and reported an antiferromagnetic (AF) ordering of the Cr^{III} magnetic moments below $T_N \approx 30$ K. Much more recently, our neutron diffraction observation of an antipolar copper sublattice below 150 K in this compound (4) suggested that the RT density smearing may be due to the Cu^I ion hopping between two off-center sites within its octahedron rather than to a static kind of disorder. The interest in these thiophosphates as a new family of layered ferroelectric-type materials, heightened lately by the discovery of a nearly polar Cu^I configuration (3) and ferroelectric behavior (5) in $CuInP_2S_6$, motivated us to reinvestigate certain aspects of the RT structure of $CuCrP_2S_6$. Neutron powder diffraction data collected below T_N also allowed us to determine the magnetic structure of the AF phase.

The RT continuous copper electronic distribution in $CuCrP_2S_6$ was satisfactorily modeled by two quasi-vertically disposed and partially filled positions, one distinctly (Cu1) and the other slightly (Cu2) shifted from the octahedral center (1). A two-fold axis through the octahedron leads to twice as many possible positions, so that the Cu1 and Cu2 occupancy ratios per CuS_6 unit may be given as 0.66 and 0.34, respectively. Refinement of the copper anisotropic thermal factors revealed appreciable values, with the Cu1 thermal ellipsoid being elongated perpendicular to the $[SCu_{1/3}Cr_{1/3}(P_2)_{1/3}S]$ layer and that of Cu2 nearly spherical. The probability of finding a copper atom in a volume element, formally called the joint probability density function (jpdf) (6), can be calculated as the weighted sum of the Fourier transforms of the Cu1 and Cu2 temperature factors. Moreover, the one-particle potential at a point $\mathbf{r}$ may be derived as

$$V(\mathbf{r}) = V_0 - k_B T \ln [\text{jpdf}(\mathbf{r})],$$

where k_B is the Boltzmann constant and T is the absolute temperature. Because the present case involves underoccupied positions, the diffraction data represents an average filling of these sites and $V(\mathbf{r})$ is a pseudo rather than a real potential (6). Although the energy values thus obtained should be interpreted with caution, the features of such a pseudo potential remain qualitatively correct.

The copper jpdf and $V(\mathbf{r})$ were calculated from the structural parameters of Ref. (1) and mapped out using the PROMETHEUS suite of programs (7); Fig. 1 displays the results. It is clear from this that there is no probability density maximum close to the octahedral center, and consequently the pseudo potential has a simple double-well shape. Note that a distance of 2.52 Å, i.e., larger than the diameter of a Cu^I ion, separates the two minima. Thus, as may be expected from the unlikeliness of a statically stable and octahedrally coordinated Cu^I (8), neither the near-center electronic density peak nor the Cu2 site corresponds to an equilibrium position. Rather, each may be indicative of a non-zero probability of finding the copper ion between the two potential minima. This is consistent with a thermal hopping model of the copper distribution which says that the RT phase is nonpolar in a

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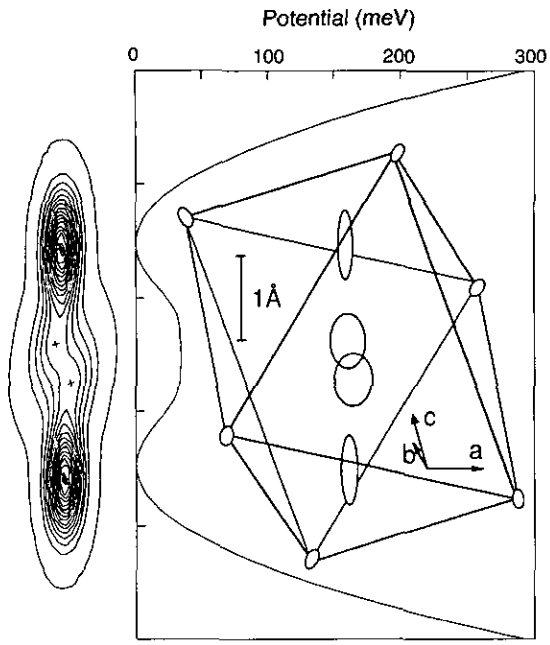

FIG. 1. The joint probability density function (jpdf) calculated from the copper positions and temperature factors of Ref. (1) (left), and the corresponding pseudo one-particle potential (right); a copper octahedron, i.e., a CuS_6 group, is also shown as a reference.

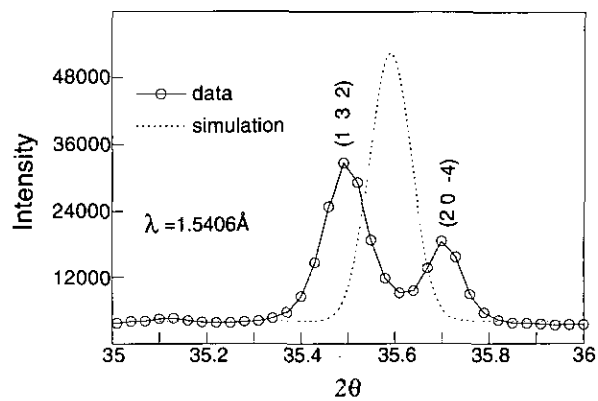

FIG. 2. The clearly resolved (1 3 2) and (2 0–4) reflections, marked "data," from the X-ray powder diffraction pattern of $CuCrP_2S_6$. The dashed "simulation" curve shows how these two peaks superpose when $\beta = \cos^{-1}(-2a/3c)$.

temporally averaged sense and that the antipolar copper sublattice appears with cooling as the energy available for hopping diminishes (4).

The monoclinic unit cell parameters of $CuCrP_2S_6$ were likewise thought to merit more precise measurement. This is important for a reliable characterization of the chalcogen stacking distortions in $MM'P_2X_6$ induced by the cation size difference (9) and described in terms of the deviations of the quantities b/a and $\cos^{-1}(-2a/3c)$ (10) from their respective ideal values $\sqrt{3}$ and β: the first represents in-plane, and the second out-of-plane packing deformations. Aside from their usefulness in the comparative study of the various phases of the series, these effects presumably evolve with temperature and may provide a consistency check on other structural changes that occur during a transition.

The RT X-ray powder diffraction pattern of $CuCrP_2S_6$ was obtained using $CuK\alpha_1$ radiation and an INEL 120° curved linear detector calibrated with $Na_2Ca_3Al_2F_{14}$. The least-squares cell parameter refinement was performed on the peak positions determined by a careful profile fit of each reflection (11). A comparison of our parameters, a = 5.9217(5) Å, b = 10.2592(8) Å, c = 13.3721(10) Å, and β = 106.705(14)°, with those of Ref. (1), a = 5.916(1) Å, b = 10.246(2) Å, c = 13.415(5) Å, and β = 107.09(3)°, shows that the cell volumes and b/a ratios from the two parameter sets are equal within experimental accuracy. On the other hand, whereas with the older parameters $\cos^{-1}(-2a/3c)$ calculates to β, our parameters yield 107.1711(3)°, which is larger than the measured angle. A signature of our smaller β value is the splitting of the strong (132) and (20–4) peaks, which was quite obvious in our diffraction pattern (Fig. 2); the parameters of Ref. (1) lead to overlapping 2θ's for these reflections, so it would seem that they were not resolved in the earlier work. The out-of-plane packing deformations in $CuCrP_2S_6$ are thus stronger than had been suspected.

Last, for additional insight into the Cr^{III} AF ordering, neutron powder diffraction data were collected at 11 K (12); a pattern at 64 K characteristic of the antipolar low temperature (LT) $CuCrP_2S_6$ phase was also measured (4). A glance at the two data sets (Fig. 3a) reveals the presence of new peaks at 11 K, notably one which indexes as (001), in violation of a reflection condition of the space group Pc ([00L] for $L = 2n$) within which the LT nuclear structure was described. This (001) peak implies the appearance of a sublattice with a periodicity given by the second-nearest-neighbor layer spacing, in agreement with an AF arrangement of planes formed by ferromagnetically coupled spins (1). The magnetic nature of this sublattice is attested to by the form of the (001) integrated intensity versus T curve (Fig. 3b). The presence of the (001) peak also indicates that the spins cannot be parallel to c^*. Furthermore, refining the magnetic structure (13) with all three components of the magnetic moment $\mathbf{m}$ as free parameters converges to a null m_z solution. Constraining $\mathbf{m}$ to lie in the a–b plane leads to $|m_x| = 1.6(2)$ and $|m_y| = 2.5(1)$ μ_B, i.e., a moment of 3.0(2) μ_B and a

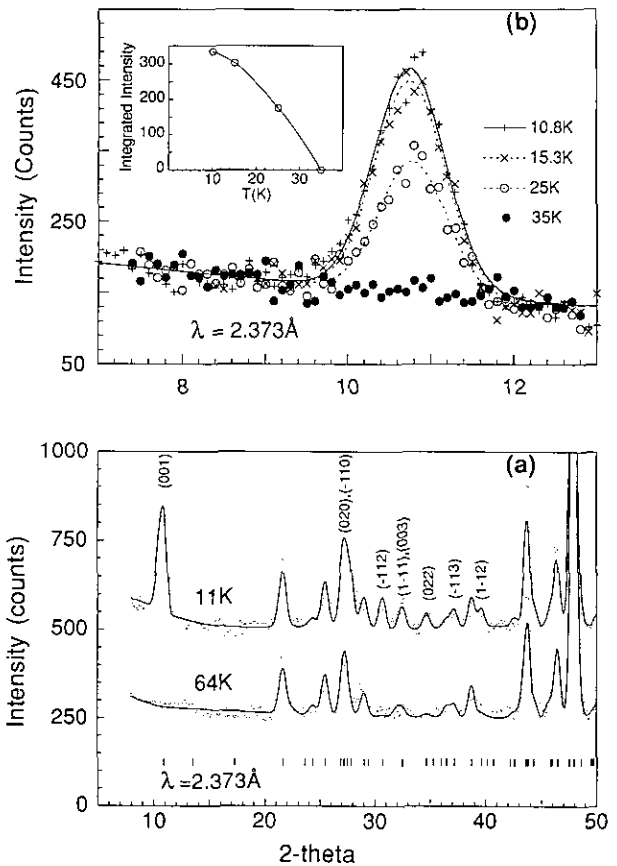

FIG. 3. (a) Comparison of the neutron powder diffraction patterns at $T = 11$ K and 64 K; $R_{wp} = 11.60\%$ and $R_{exp} = 6.77\%$ for the 11 K pattern refinement assuming nonzero m_x and m_y. The tic marks indicate the positions of the magnetic peaks and the indexation for the strongest of these is given above the $T = 11$ K diagram. (b) Temperature-evolution of the (001) magnetic peak fitted with a Gaussian; the inset plots the corresponding integrated intensity.

spin direction approximately along the diagonal of the a–b plane. Such a collinear structure accords with the occurrence of a spin-flop transition as inferred from the magnetization data of Ref. (1).

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