

Spin-density distribution in the tetragonal cluster compound $\text{Cu}_4\text{OCl}_6\text{daca}_4$

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The spin-density distribution in $\text{Cu}_4\text{OCl}_6\text{daca}_4$ (daca=diallylcyanamide), a system containing tetrahedra of Cu^{2+} ions, has been determined using single-crystal polarized neutron diffraction at temperature 10 K and magnetic field 9 T. The data have been analyzed both with a spherical atom model and using a maximum entropy reconstruction. The magnetic moment on the Cu^{2+} ion is reduced to $0.35(1)\mu_B$ and significant delocalization of spin density [$0.16(3)\mu_B$] is found within the Cu_4OCl_6 core. The experimental spin-density distribution is compared with the predictions of *ab initio* density-functional calculations.

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I. INTRODUCTION

Magnetically frustrated molecules provide an important subject for investigation both for their own sake and as the building blocks of complex two- and three-dimensional (3D) geometrically frustrated systems; the kagomé and pyrochlore lattices are examples.¹ The situation may not be trivial even when only spin degrees of freedom are involved. For example, antiferromagnetic coupling of $S=\frac{1}{2}$ spins in an isolated regular tetrahedron leads to a spin multiplet. The ground state is a nonmagnetic doubly degenerate singlet ($S_{tot}=0$), the first excited state is a threefold degenerate triplet ($S_{tot}=1$) and the state with the highest energy is a quintet ($S_{tot}=2$). These degenerate states are not, however, found in real systems, the energies of different configurations are very susceptible to perturbations and the degeneracy can be lifted by various tiny effects—higher order terms in the spin Hamiltonian, coupling of electron spins to structural and vibrational degrees of freedom, etc.

The frustrated molecular spin cluster V_{15} (Ref. 2) and the molecular nanomagnet Fe_8 (Ref. 3) are well-documented examples of systems in which lattice strains or vibrations relieve the ground-state degeneracy. The $\text{Cu}_4\text{OX}_6\text{L}_4$ system may provide yet another example. The isolated $\text{Cu}_4\text{OX}_6\text{L}_4$ units are coupled by weak van der Waals interactions to build a molecular crystal. Each molecule has a Cu_4OCl_6 core and four terminal ligands L (Fig. 1). The oxygen O^{2-} ion is at the center of the complex, it is surrounded by a tetrahedron of copper, Cu^{2+} , ions which, in turn, is enclosed by a distorted octahedron of halogen, X^- , ions. Such arrangement lead to two competing magnetic exchange paths—antiferromagnetic Cu-O-Cu and ferromagnetic Cu-X-Cu. Various terminal ionic or neutral ligands [i.e., Cl^- ; pyridine, $\text{C}_5\text{H}_5\text{N}$;⁴ and triphenylphosphine, $(\text{C}_6\text{H}_5)_3\text{PO}$ (Refs. 5 and 6)] can bond to the Cu^{2+} ions therefore the $\text{Cu}_4\text{OX}_6\text{L}_4$ family has numerous members.

Recently we have made an extensive experimental characterization of one member of this family, metal-organic $\text{Cu}_4\text{OCl}_6\text{daca}_4$ [daca stands for diallylcyanamide, $\text{NCN}-(\text{CH}_2-\text{CH}=\text{CH}_2)_2$].⁷ The bulk susceptibility, magneti-

zation, specific heat, and inelastic neutron scattering (INS) measurements cannot be explained using an unperturbed isotropic Heisenberg spin Hamiltonian. The small size of the magnetic moment at low temperatures, the bump at 12 K in the temperature evolution of magnetization and the 1.8 meV magnetic excitation in the INS spectra are compatible with clusters having a nonmagnetic ground state and antiferromagnetic exchange of ≈ 1.8 meV. On the other hand the steps in the ac susceptibility and the Schottky-type anomaly in the specific heat are indicative of low-lying magnetic states. In addition no explanation is available for the big difference between the dc magnetization measured in crystallographically equivalent, but differently developed $[110]$ and $[\bar{1}10]$ directions in single crystals. Furthermore we were

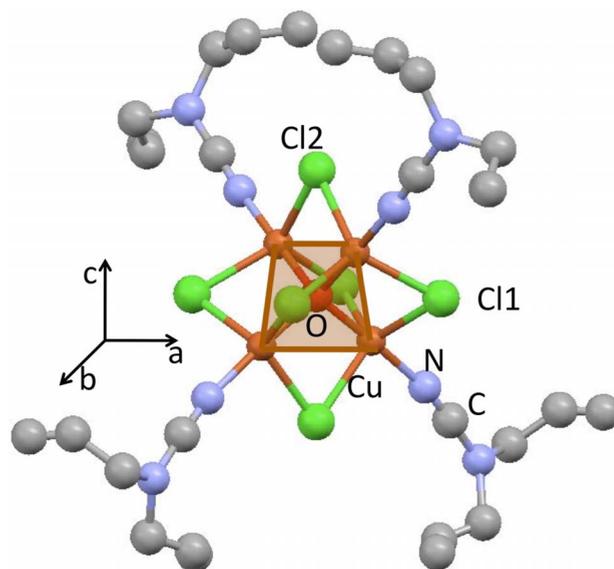


FIG. 1. (Color online) The 3D view on the molecule of $\text{Cu}_4\text{OX}_6\text{L}_4$. The Cu^{2+} ions are represented by orange and O^{2-} and Cl^- by red and green circles, respectively. Here the four branched ligands L =diallylcyanamide are presented by nitrogen (blue) and carbon (gray) atoms, hydrogens are omitted for clarity.

unable to explain these measured properties using more complex models such as a generalized spin Hamiltonian including asymmetric and/or antisymmetric exchange terms⁴ or the spin-vibrational Hamiltonian^{8–10} proposed for the $\text{Cu}_4\text{OX}_6\text{L}_4$ family. It is, however, possible that the presence of molecular vibrations and configurational disorder above $T_c=282$ K could have a strong influence on the low-temperature magnetic properties.

The present work was undertaken to determine whether the low magnetic moment observed at low temperatures is an intrinsic property of the system and whether the spin density is delocalized within the Cu_4OCl_6 core as suggested by the *ab initio* density-functional theory (DFT) calculations.⁷ To answer these questions we have made polarized neutron-diffraction measurements at 10 K on a single crystal of $\text{Cu}_4\text{OCl}_6\text{daca}_4$ magnetized by a 9 T field.

II. EXPERIMENTAL

The experiment measures the polarization dependence of the intensity of Bragg reflections from a single crystal in which magnetic moment is aligned by a magnetic field applied along the neutron polarization direction \mathbf{P} . As the induced magnetization has the same periodicity as the nuclear structure, the weak magnetic signal adds to the nuclear intensity in the Bragg reflections which, when the incident neutrons are polarized, also includes a nuclear-magnetic interference term.^{11,12} The magnetic structure factors \mathbf{F}_M are related to the measured flipping ratios R

$$R = \frac{I_+}{I_-} = \frac{|F_N|^2 + \mathbf{P} \cdot \mathbf{F}_M \mathbf{F}_N^* + \mathbf{P} \cdot \mathbf{F}_M^* \mathbf{F}_N + |F_M|^2}{|F_N|^2 - \mathbf{P} \cdot \mathbf{F}_M \mathbf{F}_N^* - \mathbf{P} \cdot \mathbf{F}_M^* \mathbf{F}_N + |F_M|^2}. \quad (1)$$

A precise knowledge of the nuclear structure factors F_N is needed to analyze the data. We therefore made an unpolarized single-crystal neutron-diffraction experiment, prior to the polarized one, to determine the structural parameters. The unpolarized diffraction experiment was performed on the TriCS diffractometer at SINQ using a neutron wavelength of $\lambda=1.18$ Å. It was found that the quality of the crystal is dramatically lowered while cooling through the order-disorder transition temperature $T_c=282$ K. Each Bragg peak splits into several peaks (Fig. 2) and this process is not reversible upon heating to 300 K. Only by slow cooling a crystal at a rate of <0.5 K/min, it was possible to obtain diffraction data of reasonable quality at low temperatures. The Bragg peaks in this case were doubled in width compared to the as-grown crystal. The lattice constants ($a=12.589$ Å and $c=12.6558$ Å at 10 K) changed significantly from their room-temperature values in agreement with synchrotron x-ray diffraction results.⁷ The integrated intensities of 776 reflections ($591I > 3\sigma I$, $\sin \theta/\lambda < 0.48$ Å⁻¹) collected at 5 K from a ≈ 10 mm³ crystal were used to refine the positions and isotropic thermal parameters of 23 independent atoms. The results of the refinement were of only moderate precision ($R_{obs}=12.7\%$, $R_{wobs}=12.67\%$) as the poor quality of the crystal severely diminished the accuracy with which the intensities of Bragg peaks at high scattering angles could be measured. The atomic parameters do not, however,

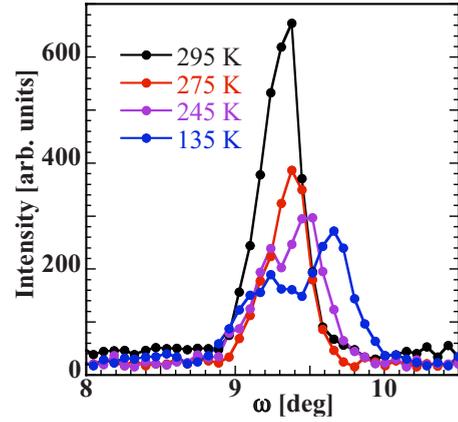


FIG. 2. (Color online) ω scans through the (222) Bragg peak while cooling the crystal.

deviate significantly from the values obtained in the low-temperature synchrotron x-ray experiment.⁷ We therefore decided to use the latter in calculating the nuclear structure factors F_N .

The polarized neutron-diffraction (PND) experiment was performed on the D3 instrument at ILL at 10 K using a neutron wavelength of $\lambda=0.825$ Å. The polarization of the incoming beam $P=0.962(5)$ was switched with a cryoflipper to be alternately parallel and antiparallel to the vertically applied magnetic field of 9 T. The crystal of volume ≈ 10 mm³ mounted with a [110] axis vertical was cooled slowly (rate 0.5°/min) to avoid cracking. The quality of the crystal is less important in this experiment as the quantity R is a ratio measured at the maxima of the Bragg peaks and not dependent on correct integration over the broad reflection curve. The flipping ratios of 83 independent reflections with $\sin \theta/\lambda < 0.3$ Å⁻¹ were measured.

III. ANALYSIS OF THE DATA AND DISCUSSION

The data were analyzed using two different techniques. In the first the spin density was modeled as the sum of spherically symmetric spin distributions centered on atomic sites and in the second a Fourier reconstruction of the spin density was made using the maximum entropy method.^{13–15}

In the atomic model all atoms in the Cu_4OCl_6 core were allowed to carry a moment. Their magnetic form factors were calculated from the radial wave functions of the valence electrons tabulated in Ref. 16. The measured data were presented as intensity asymmetries A , which, for $|F_N| \gg |F_M|$, can be approximated as

$$A = \frac{I_+ - I_-}{I_+ + I_-} = \frac{2|F_M| \sin^2 \alpha \cos(\phi_N - \phi_M)}{|F_N|}. \quad (2)$$

Here $F_N = |F_N|(\cos \phi_N + i \sin \phi_N)$ and $F_M = |F_M|(\cos \phi_M + i \sin \phi_M)$ are complex nuclear and magnetic structure factors, α is the angle between the scattering vector and the polarization direction. Refinement of the magnetic moments on the atoms in the Cu_4OCl_6 core with respect to the asymmetries using the CCSL code¹⁷ gave a magnetic moment of $1.70(3)\mu_B/\text{Cu}_4\text{OCl}_6$ ($\chi^2=2.1$, $R_w=21.02\%$). The majority

TABLE I. Magnetic moment in [μ_B /atom] within the Cu_4OCl_6 core from previously published DFT calculations, Ref. 7, M_{calc} , and refined from present polarized diffraction data, M_{exp} .

Atom	M_{calc}	M_{exp}
Cu	0.584	0.35(1)
O	0.442	0.08(2)
Cl (basal)	0.084	0.06(1)
Cl (apical)	0.090	0.02(1)

of the moment is located on the Cu^{2+} ions but is only $0.35(1)\mu_B/\text{Cu}^{2+}$. This analysis clearly indicates a transfer of unpaired electron density to the oxygen in the center of the Cu_4OCl_6 core and to the four Cl^- ions at the base of the distorted octahedron (see Table I).

Further delocalization of the spin density within the molecule, not included in our atomic model, is possible. A model-free reconstruction of the spin-density distribution was therefore made using a maximum-entropy algorithm. In the present noncentrosymmetric case (space group $P\bar{4}2_1c$) the measured flipping ratios are not linearly related to the Fourier transform of the reconstructed spin-density map. A software based on the MEMSYS package,¹⁸ described in Ref. 15, was used. The maximum entropy reconstructions are consistent with the atomic model and may indicate even stronger spin delocalization. As presented in Fig. 3, the spin density is delocalized between the Cu^{2+} ions (bottom left), within the core of the molecule at the O^{2-} (bottom middle), Cl^- basal ions (bottom right), and possibly even along the $\langle 111 \rangle$ directions between the molecules (top).

The results of the polarized neutron-diffraction experiment are in quantitative agreement with the previous bulk measurements. The magnetic moment of $1.70(3)\mu_B/\text{Cu}_4\text{OCl}_6$ is consistent with the dc magnetization value $2\mu_B/\text{Cu}_4\text{OCl}_6$ (Ref. 7) for $H\parallel[110]$. Analysis of the data with both the atomic and maximum entropy models clearly confirms the delocalization of spin density predicted by the DFT calculations.⁷

However a detailed comparison of the values obtained from the DFT calculation with those from the PND experiment presented in Table I reveals several discrepancies. First, the DFT calculation gives a significantly larger transfer of unpaired electron density to the oxygen in the center of the Cu_4OCl_6 core compared to that measured. Such a discrepancy has been found before, in particular among Cu^{2+} compounds,^{19–22} it is usually attributed to using different models to determine experimental and theoretical spin populations. Additionally in this particular case the precision of the PND data was limited by deterioration of crystal quality below T_c and did not justify interpretation beyond the spherical approximation. Second, the DFT calculation and the PND experiment give different magnetic moments per molecule. This is not unexpected as the two methods probe different states. The DFT calculation determines the ground state of the cluster and lacking resolution in the millielectron volt range it identifies this as the quasiquintet. We use the prefix “quasi” to emphasize that the simple Heisenberg spin Hamiltonian model is not valid. For the PND measurement on the

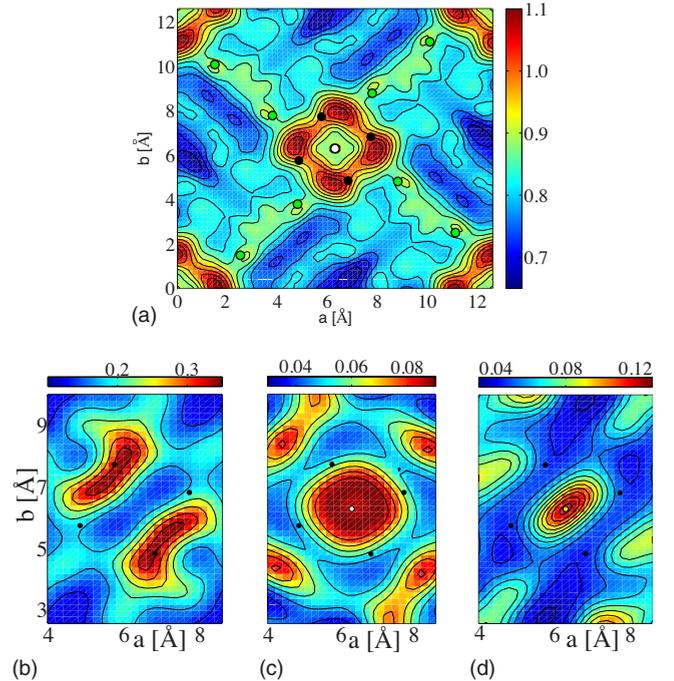


FIG. 3. (Color online) Spin-density distribution in $\text{Cu}_4\text{OCl}_6\text{daca}_4$ reconstructed by MAXENT, represented as a bound projection orthogonal to z . Top: bound projection with z ranging from 0 to 12.6558 Å. Bottom right: detail near the Cu^{2+} ions; bottom middle: detail around the O^{2-} ion; and bottom left: detail around the Cl^- apical ion. The Cu^{2+} , O^{2-} , and Cl^- basal ions are marked by black, white, and green circles, respectively.

other hand the relevant state at 10 K and 9 T is probably the quasitriplet whose energy is lowered due to the Zeeman effect.

It is still unclear why bulk the magnetization is different along the crystallographically equivalent $[110]$ and $[1\bar{1}0]$ directions. A crystal grown below the order-disorder crossover, if it were possible, would determine whether or not this anisotropy originates from defects introduced during the synthesis at room temperature.⁷

IV. CONCLUSIONS

The polarized neutron experiment performed at 10 K and 9 T has shown that the low magnetic moment $0.35(1)\mu_B$ per Cu^{2+} and $0.16(3)\mu_B$ delocalized within the Cu_4OCl_6 core is an intrinsic property of the $\text{Cu}_4\text{OCl}_6\text{daca}_4$ crystal. The low value of magnetic moment suggests that at 10 K in 9 T we are probing mainly the quasitriplet excited state given by the isotropic spin Hamiltonian. Bulk measurements, inelastic neutron scattering, and molecular-dynamic calculations⁷ have shown that the Hamiltonian must be more complex. An inelastic polarized neutron-scattering experiment should be able determine whether the spin-vibrational Hamiltonian is the appropriate model. However another member of the $\text{Cu}_4\text{OX}_6\text{L}_4$ family should be chosen for such an experiment since in $\text{Cu}_4\text{OCl}_6\text{daca}_4$ itself absorption and incoherent scattering of neutrons are severe.

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