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Hierarchical geometric frustration in $La_3Cu_2VO_9$

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Abstract

The crystallographic structure and magnetic properties of $La_3Cu_2VO_9$ were investigated by powder neutron diffraction and magnetization measurements. The compound materializes geometric frustration at two spatial scales, within clusters and between clusters, and at different temperature scales. It is shown by exactly solving the Hamiltonian spectrum that collective spins are formed on each cluster at low temperature before inter-cluster coupling operates.

1. Introduction

The physics of geometrically frustrated magnets has attracted a lot of attention in the recent years, because of the number of novel phases they would generate either in toy models of statistical physics or in condensed matter realizations [1, 2]. The field of molecular magnetism has also raised strong interest by offering a unique playground for testing quantum physics fundaments and simultaneously being at the forefront of applied research [3, 4]. In this work, we investigate a two dimensional magnet, the layered oxide $La_3Cu_2VO_9$, which exhibits many of the properties one may encounter in frustrated as well as in molecular magnets. The only magnetic ions in this compound are the Cu^{2+} ions, which are antiferromagnetically coupled and form planar clusters of four corner-sharing triangles [5, 6], thus materializing geometric frustration of quantum spins $1/2$ in a nanomagnet. These clusters are themselves antiferromagnetically coupled, leading to a novel two dimensional frustrated structure, which can be seen as a triangular lattice of nine-spin units similarly as the Kagomé lattice is seen as a triangular lattice of three-spin units (triangles) (see figure 6 in [6]). As explained later on, inter-unit couplings are much weaker than intra-unit couplings. This offers the unique opportunity to study geometrical frustration with two spatial scales, themselves resolved by two different energy scales.

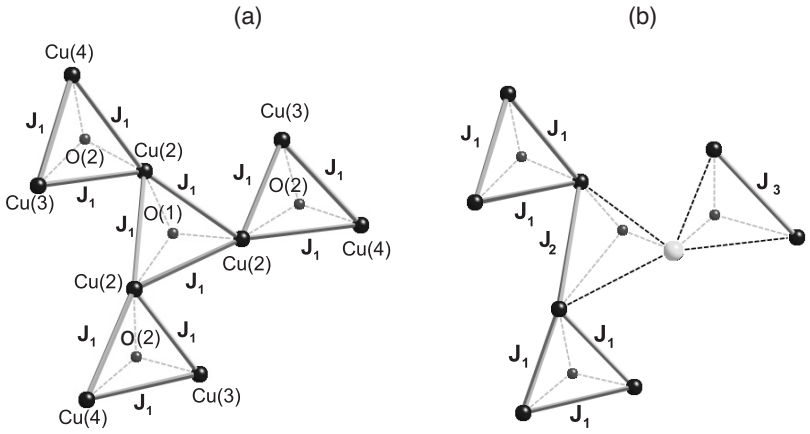

Figure 1. Atomic arrangement in the nine-spin clusters (a) and eight-spin clusters (b), calculated with DFT methods, of the Cu (large black), V (large grey) and O (small black) atoms. Labelling of the different superexchange interactions as discussed in section 3.

We report in this paper some results of our current investigations of the $La_3Cu_2VO_9$ oxide [7], concerned with its crystallography and its magnetism, and provide a quantitative analysis of its magnetic properties, within the temperature where these are answerable to independent clusters.

2. Experimental details

2.1. Crystallographic properties

The $La_3Cu_2VO_9$ oxide crystallizes in the hexagonal $P6_3/m$ space group with lattice parameters $a = b = 14.395$ Å and $c = 10.657$ Å at 300 K. The $LaO_{6/3}$ layers alternate with $(Cu/V)O_{3/3}$ layers, illustrating the 2D character of the structure. Within these, the Cu^{2+} ions are distributed over three inequivalent sites Cu(2), Cu(3) and Cu(4) (following the site labelling of [6]), having respectively distorted trigonal bipyramidal (Cu(3), Cu(4)) and tetrahedral (Cu(2)) coordination environments. These form the planar clusters of nine spins 1/2 made of four corner-sharing triangles (cf figure 1(a)). Each cluster is centred at the vertex of a 2D triangular lattice. On examining the crystal structure, we observe that there are two short intralayer exchange paths respectively mediated by one and two oxygens while the shortest interlayer exchange is mediated by two oxygens. We would then expect that the intralayer coupling is larger than the interlayer one.

Polycrystalline $La_3Cu_2VO_9$ samples were synthesized by a sol–gel method. The stoichiometric metallic cations were dissolved in nitric acid before being complexed by addition of EDTA (ethylenediaminetetraacetic acid) in a controlled pH solution. This solution was polymerized and then heated at 700 °C to eliminate the organic constituents. The resulting powders were annealed during 15 days at 1010 °C. The structural quality of the samples were checked at 300 K by x-ray analysis. The crystal structure was confirmed and no impurities were detected.

A high resolution powder neutron diffraction experiment was conducted on the D2B diffractometer at the Institut Laue–Langevin, to get further insights about the crystal structure and because in stoichiometric proportions a slight excess of vanadium ions results in the

presence of substitutions of V^{5+} ions for Cu^{2+} ions. The pattern collected at 3 K was refined by allowing V substitution on each Cu site, alternatively. The fit is slightly better when the Cu(2) site is substituted by approximately 9% of V and the Cu(3) and Cu(4) sites are unsubstituted, which is compatible with the result obtained in [6]. The deduced statistical population of clusters consists then in 66% nine-Cu clusters, 30% eight-Cu clusters and 4% seven-Cu clusters, the six-Cu clusters being practically inexistent. However, the very weak sensitivity of the fit to the Cu^{2+} site occupancy underlines the need of a further detailed investigation.

Electronic structure calculations were performed, within the density functional theory using the VASP package [8], with periodic boundary conditions and a unit cell containing 130 atoms, including two clusters located in the two $(Cu/V)O_{3/3}$ layers at $z = 1/4$ and $3/4$. These suggested that the seven-Cu clusters are energetically unfavoured and that the compound should in effect be considered as made of the clusters shown in figure 1, in the proportion of two-thirds nine-Cu clusters and one-third eight-Cu clusters. We also summarize in this figure the type of expected superexchange interactions within the clusters.

2.2. *Magnetic properties*

Magnetization measurements were performed at the Laboratoire Louis Néel on a commercial Quantum Design MPMS SQUID magnetometer, from 2 to 350 K under a magnetic field up to 5 T, and by the axial extraction method on purpose built magnetometers, which are less sensitive but allow measurements in wider ranges of temperature, up to 800 K, and of magnetic field, up to 10 T.

The isothermal magnetization curves, recorded at various temperatures, do not show any obvious signature of a transition towards a long range magnetic order, although there may be a slight shape difference between the magnetic isotherms at 1.6 and 3 K [7]. The magnetic linear susceptibility $\chi = M/H$ was recorded under a 0.1 T magnetic field where the isothermal magnetization is still linear. Its inverse is shown as a function of the temperature in figure 2(a). This last curve has a peculiar shape, made of three quasi-linear regions at low (I), medium (II) and high (III) temperatures with different slopes. It was earlier suggested [6] that these would emerge from the paramagnetic Curie–Weiss behaviour $\chi = C/(T - \theta)$ of distinct magnetic entities interacting with different interactions (accounted for by the Curie–Weiss temperature θ). $C = ng^2\mu_B S(S+1)/3k_B$ ($g = 2$) was evaluated per cluster with n the number of magnetic entities in the cluster and S their spin value.

In a preliminary step we adopted the same analysis. We show in figure 2(a) the results of our analysis. The numerical values of n, θ, the effective moment $\mu_{\text{eff}} = g\sqrt{S(S+1)}$, and the temperature range of the fit corresponding to the linear portion of regions (I) and (III) are all reported in table 1. Assuming $S = 1/2$, the slope of the high temperature region (III) is well described above 500 K by the Curie–Weiss behaviour with $n = 8.667$ ($=2/3 \times 9 + 1/3 \times 8$), which takes account of the Cu/V substitution. The resulting large negative Curie–Weiss temperature for this regime, $\theta = -327$ K, denotes a strong intra-cluster antiferromagnetic coupling between these spins.

Concerning the intermediate temperature region (II), the Curie–Weiss analysis leads to $n \simeq 4$ spins $1/2$ per cluster. In section 3, our analysis through exact solution of the cluster Hamiltonian shows however that this does not have any physical meaning since no collective magnetic entities are actually formed [7].

Unlike in [6], we found it more difficult to isolate a linear regime in $1/\chi$, which rather presents a continuous curvature (inset of figure 2(a)). A forced Curie–Weiss fit in the reduced temperature range below 15 K yields approximately one spin $S = 1/2$ per cluster, which

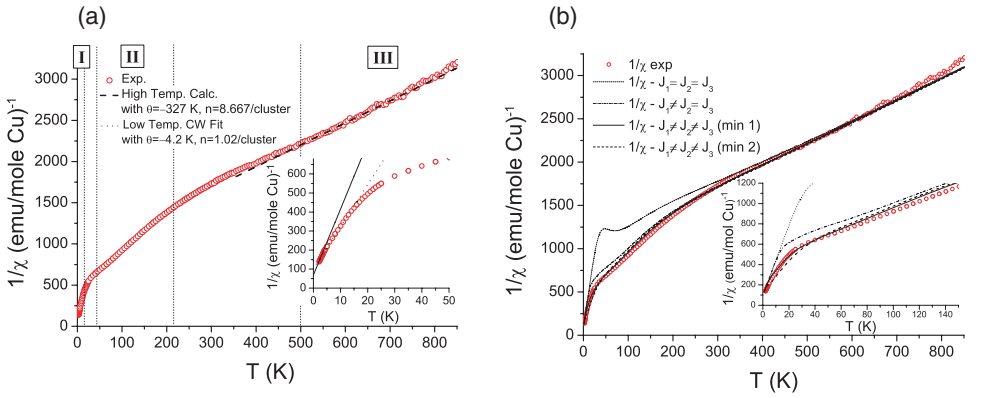

Figure 2. (a) Inverse of the linear magnetic susceptibility of $La_3Cu_2VO_9$ (hollow circles) measured in 0.1 T. The dashed line results from a Curie–Weiss fit at high temperature. The vertical dotted lines materialize the three distinguished regions of quasi-linear magnetic behaviours. The inset shows details of the thermal variation in region (I) with the forced Curie–Weiss fit (dotted line) and the expected behaviour for an ensemble of two-thirds nine-Cu clusters and one-third eight-Cu clusters (continuous line). (b) Comparison of the inverse of the measured susceptibility (circles) and of the calculated one (lines) from different models of intra-cluster interactions taking into account eight-Cu and nine-Cu clusters: $J_1 = J_2 = J_3$, $J_1 \neq J_2 = J_3$, $J_1 \neq J_2 \neq J_3$ (see figure 1 (b) and section 3).

(This figure is in colour only in the electronic version)

Table 1. Curie–Weiss parameters resulting from the fit of the inverse susceptibility in the two quasi-linear regimes at low and high temperature.

Region	T range (K)	θ (K)	μ_{eff} (μ_B)	n
I	2–11	-4.2 ± 1.1	1.732	1.02 ± 0.19
III	500–850	-327 ± 73	1.732	8.667

would suggest that the magnetic entities in the low temperature range are collective pseudo-spins, resulting from the entanglement of the wavefunctions of the paramagnetic spins within each cluster at high temperature. Since $\theta = -4.2$ K, these pseudo-spins would be weakly antiferromagnetically coupled to each other. We notice that this θ value is by two orders of magnitude smaller than that in region (III), namely inter-cluster coupling is much weaker than intra-cluster coupling. A main problem with this low temperature analysis is that $n = 1.02$, which is inconsistent with the existence of eight-Cu clusters, for which a collective pseudo-spin $S = 0$ would be expected. We notice however that the slope of $1/\chi$ increases, i.e. n decreases, when the temperature decreases, which would suggest the existence of thermally populated low energy magnetic excitations for eight-Cu clusters. This requires a more stringent analysis of the magnetism of the clusters through exact computation of model Hamiltonians.

3. Hamiltonian analysis

Each plane of $La_3Cu_2VO_9$ is a triangular lattice of nine-spin and eight-spin clusters with localized spins 1/2 on each Cu coupled through superexchange via interstitial oxygens. At first glance, the experimental study reveals that two sets of antiferromagnetic exchange interactions are effective in this system. The strongest one couples Cu^{2+} ions within a cluster, while the weakest one couples clusters together. From the susceptibility measurements, the latter

is two orders of magnitude smaller. As a consequence, there are two scales of frustration. We shall now focus on the single cluster physics and leave for a forthcoming publication [7] the inter-cluster coupling, as the magnetic properties of $La_3Cu_2VO_9$ should be dominated by that of isolated clusters, at least for $T \gtrsim 2$ K. However, when comparing the calculation to the experiment, the inter-cluster coupling is taken into account within the molecular field approximation.

In a single cluster approach, the calculation of the $La_3Cu_2VO_9$ magnetic properties are obtained through exact diagonalization of the Hamiltonian matrix of the modelled system. We shall always consider a statistical ensemble of two-thirds nine-Cu clusters and one-third eight-Cu clusters. At first, the clusters are all described by the Heisenberg Hamiltonian

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \tag{1}$$

with the same antiferromagnetic exchange constant $J < 0$ limited to nearest neighbour spins $\mathbf{S}_i$ and $\mathbf{S}_j$ (figure 1). As shown in figure 2(b), the different experimental regimes of the inverse magnetic susceptibility, the fingerprint of the collective pseudo-spin formation, are not correctly reproduced in the calculation, pointing out the limitation of this simple cluster model. On scaling the calculated $\chi = (2/3)\chi_9 + (1/3)\chi_8$, resulting from the weighted average of the eight-spin, χ_8, and nine-spin, χ_9, susceptibilities to the high temperature regime (III), we get $J \simeq -385$ K as a crude estimation of the exchange interaction.

To improve the model, the distortion of the eight-Cu clusters and the subsequent change in the exchange interactions accompanying the Cu/V substitution, evidenced in the DFT calculations, was taken into account by considering three different exchange parameters as depicted in figure 1(b). The susceptibility has been calculated, by varying systematically the three exchange interaction constants and comparing results to the experimental inverse susceptibility, imposing first $J_2 = J_3$, then leaving these to vary freely with respect to each other. When $J_2 = J_3$, the best agreement is obtained for $\{J_1, J_2, J_3\} = \{1.06, 0.27, 0.27\}J$ with $J = -385$ K, (see figure 2(b)), while for $J_2 \neq J_3$, two minima in the goodness of fits were found in the $\{J_1, J_2, J_3\}$ parameter space: $\{J_1, J_2, J_3\} = \{1.06, 0.42, 0.05\}J$ (minimum 1) and $\{J_1, J_2, J_3\} = \{1.06, 0.05, 0.2\}J$ (minimum 2) with $J = -385$ K (see figure 2(b)). The model with $J_2 \neq J_3$ is an improvement over that with $J_2 = J_3$. It leads to a better agreement with the low temperature experimental behaviour (region (I)), in particular by providing a curved thermal variation of the inverse of the magnetic susceptibility. On examining the structure of the Hamiltonian spectrum, this is explained as due to the existence of magnetic excitations lying close to the collective $S = 0$ state on the eight-Cu clusters.

Actually, there is no reason to assume that the exchange in nine-Cu clusters is identical. Nevertheless, correct adequation to experiment is obtained within the $\{J_1, J_2, J_3\}$ model that takes into account only the effect of Cu/V substitutions. This suggests that the real exchange interaction couplings in the nine-Cu clusters should not differ that much from the uniform one. A detailed examination of its energy spectrum confirms that a collective pseudo-spin $S = 1/2$ does stabilize in the nine-Cu clusters at temperatures below 15 K. On computing the quantum statistical average of the square modulus of the collective spin, we also confirm that in region (II) a Curie–Weiss analysis has no meaning [7].

4. Conclusion

The $La_3Cu_2VO_9$ oxide compound is constituted of eight- and nine-spin clusters, laid out on four vertex-sharing triangles, the basic block of the Kagomé lattice. From comparison of magnetization measurements and exact diagonalization of the Hamiltonian of a spin cluster model, the low temperature stabilization on each nine-spin cluster of a collective pseudo-spin

$S = 1/2$ resulting from the entanglement of the spin wavefunctions of the nine paramagnetic spins $1/2$ at high temperature is evidenced. This opens the possibility to study the gradual coupling of these pseudo-spins $1/2$ at low temperature from the experimental as well as from the theoretical point of view and provides a unique experimental realization of dimensional crossover tuned by temperature.

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