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Valence bond state in the delafossite $YCuO_{2.5}$

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Abstract

We take advantage of the precise determination of the crystallographic structure of complex magnetic systems with localized moments to calculate their exchange interaction values using *ab initio* methods. The magnetic interactions are mapped onto a Heisenberg model whose exchange interaction terms are fitted to first-principles total energy calculations for different spin configurations. This method is well adapted to systems with well defined local moments, as is often the case in oxides. We discuss the delafossite $YCuO_{2.5}$, with triangular layers of magnetic ions without magnetic ordering, and for which the magnetic interactions are unknown. Using these *ab initio* parameters, we perform exact diagonalization, which yields a valence bond solid ground state and shows excellent agreement with experimental magnetic susceptibility, provided that the different interactions between Cu_1 and Cu_2 atoms in the same triangle are taken into account.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Several examples of peculiar physics related to quantum spins in a triangular geometry have recently been discussed: huge thermopower in Na_xCoO_2 and unexpected superconductivity in hydrated samples and the puzzling absence of ordering in $LiNiO_2$ in contrast with isomorphic $NaNiO_2$. In this work we discuss the doped delafossite $YCuO_{2+x}$ [1]. The determination of its detailed crystallographic structure [2] showed in fact that, for $x = 0.5$, oxygen ions locate at the centre of alternating sets of triangles, providing exchange O–Cu–O paths between $S = 1/2$

spins on alternating Δ chains, which have been assumed to be nearly independent. Due to the smaller Cu–O–Cu angle [1], nearest neighbour (nn) antiferromagnetic (AF) interactions were expected to be weaker than in the high temperature superconducting cuprates, but the prediction of their values was not direct.

At first sight, $YCuO_{2.5}$ appeared to be a nice realization of a sawtooth lattice. When all bonds have the same AF interaction values this lattice is known to show remarkable properties [3, 4]. Also the more realistic case of different base–base and base–vertex interactions has been studied [5]. Finally, a first determination of the exchange interactions from *ab initio* calculations [6] has led to a different picture and has allowed the absence of magnetic ordering experimentally observed down to low temperature to be justified. However, some discrepancies concerning the magnetic susceptibility led us to revisit this system considering different base–vertex nn AF interactions, as suggested by the chemistry of this compound. The physics is significantly changed and good agreement is now found with the experimental susceptibility.

2. Model for magnetic interactions in delafossites

As we have shown in [6], we can write the Hamiltonian of the doped delafossite as

$$H = H_0 + \tfrac{1}{2}\sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j, \tag{1}$$

where H_0 is the electronic contribution, $\mathbf{S}_i$ is the spin on Cu site i ($S = 1/2$) and J_{ij} is the exchange coupling between the Cu moments on sites i and j. The summation is made over all lattice sites. We took advantage of the knowledge of the energies of 15 independent magnetic configurations of $YCuO_{2.5}$ calculated using first principles to determine the coupling parameters J_{ij}. The procedure for fitting the J_{ij}, the methods we used, as well as the calculated crystallographic data of our compound are described in detail in [6]. The definition of the exchange interactions in the planes containing the Cu atoms is shown in figure 1. The interactions between planes were neglected as already discussed in [6]. Let us outline that, in the previous work, both the exchange coupling between Cu_1 and Cu_2 in the same triangle were supposed to be given by the same parameter J_2; however, looking at the crystallographic structure, the two bonds between Cu_1 and Cu_2 atoms are clearly different. In the present work, we raise this approximation by introducing a new parameter J_2' (see figure 1 for definition).

Then, the magnetic interactions have been estimated to be:

$$J_1 = 19, \qquad J_2 = 57, \qquad J_2' = 15, \qquad J_3 = -18, \qquad J_4 = -15, \qquad J_5 = 1$$

where the values are in meV and a positive sign corresponds to an AF exchange. The major difference with respect to our previous Hamiltonian is an important increase in the magnitude of J_2 and a decrease in the weight of J_3, as well as a strong influence of the difference between the Cu_1 and Cu_2 distances in a triangle, given that J_2 is four times as large as J_2'. Signs of all coupling interactions and the amplitude of J_1, J_4 and J_5 remain unchanged. As shown in figure 1, the Cu lattice is equivalent to a lattice of weakly frustrated ladders.

Let us discuss qualitatively the values of the exchange parameters in connection with the density of magnetization (figure 1). First of all, we notice that the Cu_1 atoms, sharing two bonds with oxygen atoms, display a localized magnetic moment, while Cu_2 atoms sharing a single bond with an oxygen, develop a rejection of the charge density in the empty region which is not affected by the oxygen doping. This lobe is spin-polarized and increases the spatial extent of the magnetic moment located on Cu_2 atoms. In order to compare the magnitude of the exchange parameters, let the interaction $J_1 = 19$ meV between two localized Cu_1 moments,

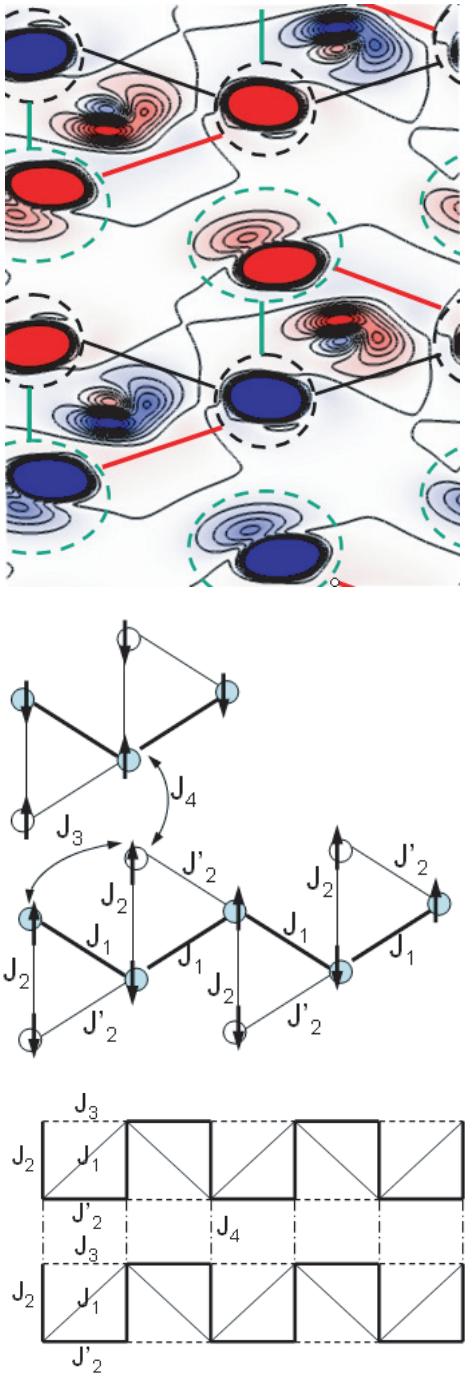

Figure 1. Density of magnetization in a (001) plane containing the Cu atoms. Cu_1 and Cu_2 atoms are enclosed in dashed black and green circles, respectively (web version) or dashed dark and grey circles, respectively (print version). Inside one-third of the triangles formed by the Cu atoms we spot the oxygen atoms by the peculiar shape of the induced magnetic moment they carry: three lobes whose spin-polarization is imposed by its nearest Cu atom. The definition of the exchange couplings is added. From the magnetic point of view, this is equivalent to frustrated ladders which are coupled in a 2D plane.

separated by a distance $d_{1-1} = 3.33$ Å, be our reference. As J_1, J_2 and J_2' present the same super-exchange scheme via the central oxygen atom enclosed in the triangle that they form (figure 1), the larger amplitude of $J_2 = 57$ meV may be attributed to the fact that the distance d_{1-2} is the shortest at 3.22 Å, while the smallest interaction, $J_2' = 15$ meV, corresponds to the longest distance $d_{1-2'} = 3.45$ Å. Also the Cu–O–Cu angles are different and influence the superexchange interaction. As regards to the direct J_4 and J_3 couplings, we argue that, despite the involved copper–copper distances being longer, the large spatial extent of the magnetic moment on Cu_2 pointing towards Cu_1 allows a non-negligible exchange coupling to develop close to the magnitude of J_1. Two Cu_2 atoms belonging to two different chains defined by the Cu_1 atoms (see figure 1) are so distant that J_5 is found to be an order of magnitude smaller than the other couplings. In the following, we will neglect this interaction.

Since J_2 is much stronger than the other exchange interactions, this system is made of strongly bound AF dimers which are weakly coupled through the smaller J_1, J_2', J_3 and J_4 interactions. Thus, the simplest approximation consists in taking a ground state which is a product of singlets on J_2 bonds, i.e. a valence bond solid (VBS). For instance, for decoupled ladders (neglecting J_4 and J_5), this is an *exact* eigenstate provided that $J_1 = J_3 + J_2'$ (similar to the Majumdar–Ghosh case, see [7]).

3. Exact diagonalization: magnetic susceptibility

We have performed exact calculations on $2 \times L$ ladders. Indeed, in order to be able to perform a finite-size analysis, we consider decoupled ladders, i.e. we neglect J_4. The results show that the correlation length is indeed very small in that system, which will justify our approximation. Depending on the physical quantity we need, we can either compute the full spectrum (for lengths $L \leqslant 8$) or compute only the ground state by using the standard Lanczos technique (for lengths up to $L = 14$).

The ground state is a singlet state and the spin gap can be evaluated easily since the exact results have almost no finite-size effects; we find $\Delta_s = 2.342 J_1 = 44.5$ meV, or equivalently 516 K. We also notice that the dispersion of the triplet excitations is very small.

By computing the full spectrum, we can plot the spin susceptibility χ versus temperature. Results are shown in figure 2 and are compared with the pure valence bond state ($N = 2$) and the experimental data. We have computed χ for various sizes (from 8 to 16 spins) and we do not observe any significant change, which indicates that the correlation length is rather short in this system. For instance, we show on the same figure 2 the χ value obtained by considering an isolated rung ($N = 2$) and which is very similar to the exact data obtained on a ladder. Note that the temperature scale is fixed by using the *ab initio* $J_1 = 220$ K. We observe a qualitative agreement between all data; in particular the location of the maximum can be explained by the model and is around $T_m = 1.74 J_1 = 380$ K, close to the experimental value (around 500 K). In the experimental data, the downturn at low temperature is due to impurities and so is not relevant; removing this contribution, the low-temperature behaviour is rather consistent with both calculations, and then with the calculated spin gap.

By computing the ground state, we also have access to the spin–spin correlations: this calculation confirms that the ground state is close to the VBS state: the spin–spin correlation on a rung (i.e. between two sites connected by J_2) is -0.7322, which is very close to the value expected for a pure singlet -0.75. This indicates that the ground state can be viewed as a product of a singlet on J_2 rungs. Also we note that the average correlations are ferromagnetic (resp. AF) between spins on the same leg (resp. opposite legs). Both correlations decay exponentially with distance as expected for a gapped system, and we can estimate the correlation length to be 0.475 lattice spacing, which is indeed very short. Within the same leg

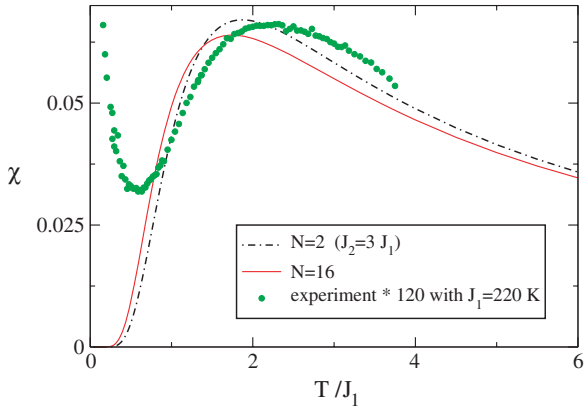

Figure 2. Spin susceptibility versus T/J_1 obtained for a rung ($N = 2$) and for a 2×8 ladder. We checked that the finite-size effects are negligible since the correlation length is very short. By comparison, the experimental data are plotted in arbitrary units along the vertical axis *but* using the *ab initio* value $J_1 = 220$ K along the horizontal axis.

the nn correlations are different if the spins interact through J_2' or through J_3: the calculated values are respectively 0.074 and 0.077.

4. Conclusion

In conclusion, we have shown that the exact calculations give a physical picture where the ground state is similar to a product of singlets on J_2 bonds. Therefore, there is a large spin-gap (45 meV according to exact diagonalization) and the correlation length is very short (less than 0.5 lattice spacing). This explains why there are almost no finite-size effects in all our computations. Still, the inter-rung couplings give rise to a small dispersion of the triplet branch and we have shown that the spin–spin correlations are ferromagnetic (resp. AF) between spins on the same leg (resp. opposite legs). Concerning the spin susceptibility, by using the *ab initio* parameters, we obtain a qualitative agreement between our data and the experimental ones [8, 9]. In particular, the location of the maximum is consistent with our estimate and also the large value of the spin gap. In fact, the next step should take into account the inter-ladder coupling J_4 which is of the same order as some intra-ladder couplings. This can be done perturbatively, but we expect that the ground state will still be close to a valence bond solid.

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