$R\mathrm{CuO}_{2.66}$ delafossites: A dilute $s=1/2$ *kagomé*-like lattice

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The hexagonal oxygen superlattice H($\sqrt{3}\times\sqrt{3}$) phase of $R\mathrm{CuO}_{2.66}$ delafossite-type compounds, R=La or Y, provides a unique example of an $s=1/2$ diluted *kagomé* system. We perform a theoretical study of the magnetic properties of this lattice, both in the insulating and the metallic cases. We attribute to the particular topology the absence of magnetic order experimentally observed down to low temperatures. The roles of longer-range interactions, defects, and quantum effects are discussed. [S0163-1829(96)51926-0]

Recently Cava *et al.*[1] have succeeded in further oxidizing the ordinary delafossite-type compounds $R\mathrm{CuO}_2$ to form new superoxides $\mathrm{YCuO}_{2+\delta}$ and $\mathrm{LaCuO}_{2+\delta}$, in which extra oxygen ($0.5<\delta<0.7$) is inserted interstitially into the triangular Cu planes. This opened the possibility of studying CuO lattices with a different geometry, but a similar doping level as the high-T_c compounds: the physical properties turned out to be quite different.[1–3] The $\delta=\frac{2}{3}$ concentration is particularly interesting: structural studies[1,4] showed that an O-ordered hexagonal superlattice H($\sqrt{3}\times\sqrt{3}$) occurs and, since Cu-Cu superexchange interactions are mediated by the O atoms, this yields the effective lattice depicted in Fig. 1. If only nearest-neighbor (nn) interactions are considered this Cu-network is topologically equivalent to the *kagomé* lattice,[3] while differences appear for longer-range interactions.

There are few experimental examples of *kagomé* lattices: $\mathrm{SrCr}_{8-x}Ga_{4+x}\mathrm{O}_{19}$ with spin $s=\frac{3}{2}$,[5] and usually described by the dense *kagomé* model.[6] The organic radical system of (*m*-N-methylpyridinium α-nitronyl nitroxide) X^- has been recently proposed as a spin $s=1$ *kagomé* antiferromagnet (AF) at very low temperatures.[7] As the case of ^{3}He adsorbed on graphite remains controversial,[8] oxidized delafossites would be a first example of $s=\frac{1}{2}$ *kagomé* AF, for which quantum spin liquid properties are expected to be enhanced.

For $\delta=\frac{2}{3}$ the formal valence of Cu is 2.33 in average, which corresponds to 2 magnetic Cu^{2+} ions for each nonmagnetic Cu^{3+} ion. It is not clear from experiment if these compounds are intrinsically insulating or metallic.[1] Band-structure calculations[9] have shown that the density of states at the Fermi level is predominantly composed of $3d_{3z^2\text{-}r^2}$ orbitals (43%), consistent with soft-x-ray-absorption data.[1] In such a case the spin-orbit interaction induces a planar magnetic anisotropy,[10] giving to the spins an XY character. Due to the different orbitals involved, the effective interaction between Cu sites in the plane is expected to be two orders of magnitude smaller in delafossites,[1,11] than in the square planar Cu-O lattice of high-T_c compounds. Nevertheless it is notable that no magnetic ordering has been observed[3] down to 100 mK.

We study here the magnetic properties of this dilute *kagomé*-like lattice, with nn AF XY interactions between the $s=\frac{1}{2}$ spins, emphasizing the crucial role of the topology in the lack of magnetic ordering. We first discuss the case in which the $\frac{1}{3}$ Cu^{3+} ions are fixed. Quantum magnetic effects are shown to stabilize a different ordering of the magnetic sites than the one that would result from the Coulomb interaction between them; in none of these cases is an ordered long-range (LRO) magnetic structure for the Cu^{2+} ions obtained. As the classical ground state is strongly degenerate we study the effect of interplane and in-plane next-nearest-neighbor (nnn) interactions. Depending on the sign of these interactions different LRO structures are stabilized, but the transition temperatures are expected to be extremely low. A possible connection between the theoretical properties of this lattice and experimental results on R=Y,La delafossites $R\mathrm{CuO}_{2.66}$ is made. We conclude that no magnetic LRO can be stabilized in the insulating phase. Also in the metallic case a disordered state is obtained for the parameter values expected for these systems.

Insulating phase. For nn J_1 interactions the difference with most previous *kagomé* studies is the presence of $\frac{1}{3}$of nonmagnetic sites. Although the classical magnetic energy is lower in the dense *kagomé* lattice ($-\frac{3}{2}J_1$ per triangle), for this concentration only $\frac{2}{3}$ of the sample volume would be involved, yielding the same total exchange energy. Therefore phase separation is not favorable due to the loss of entropy in the nonmagnetic fraction of the sample. This is in agreement with the ^{63}Cu NMR results for $\mathrm{Y}_{0.99}\mathrm{Ca}_{0.01}\mathrm{CuO}_{2.65}$ of Walstedt *et al.*[2] showing that both types of sites coexist in the same crystal. Then we only consider structures with regular repartition of the Cu^{3+} sites, i.e., one nonmagnetic site on each connected triangle. In this case due to the AF interaction the other spins are antiparallel in the ground state. This yields an infinite number of disordered degenerate structures.

As we are dealing with $s=\frac{1}{2}$ particles we first look for quantum effects. If the nonmagnetic sites are fixed it can be seen in Fig. 1 that the magnetic sites always form chains. When these nonmagnetic sites are disordered, closed and open chains coexist in the lattice. Due to the topology the closed chains involve $N=6+4n$, with $n=0,1,2,\ldots$ mag-

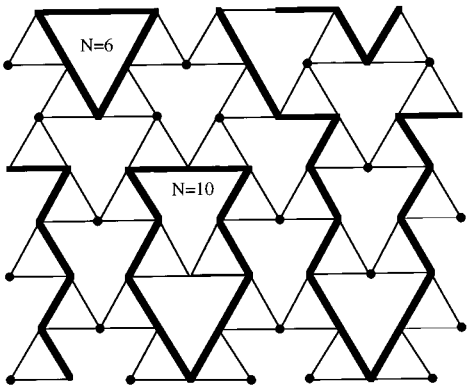

FIG. 1. Cu-O planes in the $\delta=\frac{2}{3}H(\sqrt{3}\times\sqrt{3})$ phase of $R\mathrm{CuO}_{2+\delta}$ delafossites. The Cu sites only interact though a neighboring O atom, generating this effective Cu network, with lattice parameter a. Bold lines show possible closed and open magnetic chains, for $\frac{1}{3}$ disordered fixed nonmagnetic Cu^{3+} sites, represented by the bold circles.

netic sites. For such chains the exact solution of the *XY* model is known.[12] The exchange energy per site depends on the length of the chain, yielding $E/|J_1|=-2/3,\ -0.647,\ -0.642,\ -0.640,\ldots,\ -2/\pi$ for $N=6,\ 10,\ 14,\ 18,\ldots,\ \infty$; i.e., the structure with the shortest chains has the lowest energy. (This result is still valid even if the anisotropy is not large and the Heisenberg model becomes then more appropriate.) For the concentration of interest, a structure with only chains comprising $N=6$ spins is possible and leads to a regular distribution of nonmagnetic sites similar to the one shown in Fig. 2(a). The six spins in this big triangle are in a singlet state but each of these triangles is disconnected from the neighboring ones. The lattice ground-state is nondegenerate but only short-range correlations (between spins belonging to the same big triangle) occur. On the other hand, if the Coulomb repulsion between Cu^{3+} sites becomes large, a distribution of nonmagnetic sites as shown in Fig. 2(b) will be stabilized. And this in spite of the increase of exchange energy, since only infinite magnetic chains are formed; long-range correlations will survive, but within the chains. In both cases, even if the nonmagnetic sites are ordered, the properties of the lattice will be given by the one-dimensional character of the disconnected *XY* chains. The exact solution[13] for both chains, $N=6$ and $N=\infty$, yields an enhancement of the magnetic susceptibility for temperatures higher than $|J_1|/2$.

Therefore, if only nn J_1 interactions are taken into account, no LRO structure is stabilized. However, further-neighbor interactions may induce the magnetic ordering. Two ordered structures have been discussed in the literature for the *kagomé* lattice (others exist but with larger periodicity): the equivalent of the $q=\sqrt{3}\times\sqrt{3}$ and $q=0$ structures are depicted on Fig. 2, and called A and B, respectively. In structure A, Fig. 2(a) the nn nonmagnetic sites are homogeneously distributed forming disconnected triangles of parameter a. In structure B, Fig. 2(b), the nonmagnetic sites form instead a larger triangular lattice with parameter $a\sqrt{3}$. In the absence of other interactions, all spins belonging to the same $N=6$ or $N=\infty$ chain can be turned continuously within the plane without energy cost. In the A structure only the closed modes are still present, while in the B structure, only the

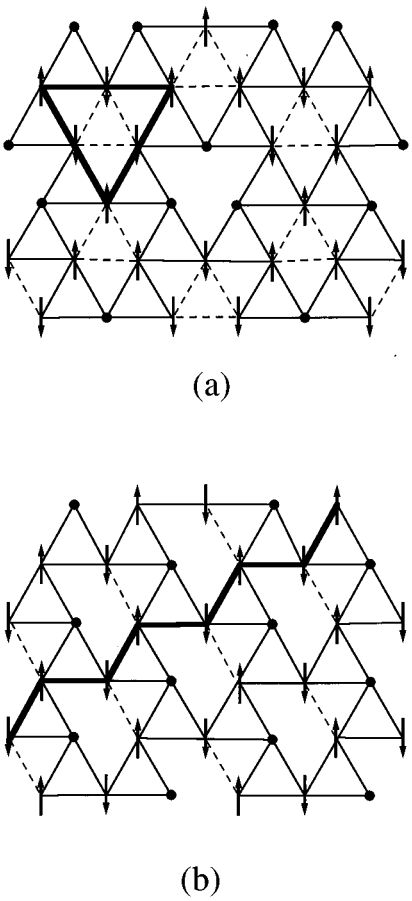

FIG. 2. Dilute ($\delta=\frac{2}{3}$) ordered magnetic structures stabilized by J_2 interactions indicated as dashed bonds, in the insulating case. (a) A structure deduced from the $q=\sqrt{3}\times\sqrt{3}$ *kagomé* structure. (b) B structure derived from the $q=0$ *kagomé* structure. Bold lines indicate closed (open) modes for the A (B) structure. For $J_2=0$, since the triangles in (a) [the chains in (b)] are disconnected, there is no magnetic LRO.

open, crossing the entire lattice, modes of the usual *kagomé* lattice are preserved.

Although the distance between Cu planes is 5–6 Å and the fact that the three-dimensional Cu lattice is not built by a simple translation parallel to the z axis,[1] the important $3d_{3z^2-r^2}$ orbital character leads us to consider the effect of interplane interactions, J'.[11] Each primitive cell of these hexagonal compounds contains two formula units: the real lattice is obtained by alternating the Cu planes, with the Cu triangles in opposite orientation.[1] Different magnetic stackings for two neighboring Cu planes are possible, leading to different interplane exchange energies. Interplane interactions play no role in the stabilizing of the B structure. In contrast, the A structure can be stabilized by ferro or AF interplane interactions, depending on the magnetic stacking of the planes, in both cases the energy gain being $|J'|$ per site.

We call J_2 the exchange interaction between nn Cu^{2+} sites in the same plane that are not connected by an in-plane additional oxygen (see Fig. 2). Due to their distance these in-plane nnn J_2 interactions are expected to be the largest ones after the J_1 interactions. This definition does not coin-

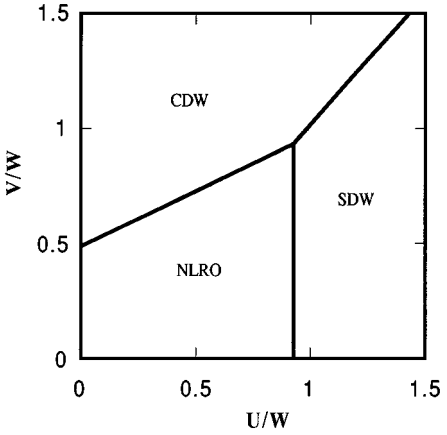

FIG. 3. Phase diagram of the new effective lattice in the metallic case: RPA calculation for a filling of $\frac{2}{3}$ Cu^{2+} magnetic ions. See text.

cide with the one of the *kagomé* lattice: the distances and the number of nnn are different. However, in both cases nnn interactions have similar effect: a ferromagnetic interaction stabilizes the $q=\sqrt{3}\times\sqrt{3}$ of the *kagomé* lattice, or the A structure of our new network, while an AF one stabilizes the $q=0$ or B structure, respectively.

We have also performed a detailed study of the influence of defects on the magnetic ordering; we summarize here the main conclusions. Relevant defects can be classified in two categories:

(i) Defects induced by the nonstoichiometry: additional nonmagnetic sites ($\delta>\frac{2}{3}$) have no effect on the magnetic LRO. However, additional magnetic Cu^{2+} sites ($\delta<\frac{2}{3}$) will change the magnetic configuration: some triangles will have three magnetic sites and the interaction energy will then be minimized by the 120° structure in these triangles. For the A structure additional Cu^{2+} sites create closed loops of magnetic defects (i.e., with spins with different orientation with respect to the rest of the lattice). For the B structure an additional magnetic moment will generate two infinite lines of magnetic defects destroying the magnetic LRO.

(ii) Defects caused only by magnetic disorder: an infinite number of disordered magnetic structures can be generated without modifying the position of the nonmagnetic sites, e.g., starting from the A (B) structure, open (closed) modes will not change the energy but will generate disorder.

We conclude that longer-range interactions can stabilize the magnetic LRO in the insulating phase but, as J' and J_2 are expected to be considerably weaker than J_1, the transition temperatures would be very low. Furthermore, defects go against this eventual ordering.

Metallic phase. Figure 3 displays the phase diagram for $\delta=\frac{2}{3}$ filling (i.e., $\frac{1}{3}$ per spin direction), obtained within the random phase approximation (RPA). The Hamiltonian considered includes the kinetic energy of $d_{3z^2-r^2}$ electrons in the effective lattice of Fig. 1, intraatomic and interatomic Coulomb repulsions U and V, respectively. If t is the effective hopping between O-connected nn Cu sites ($t<0$), the bandwidth is $W=6t$. Both U and V interactions have been linearized, this calculation can therefore be applied for moderate values of these parameters; details will be given elsewhere. Increasing U and V two different instabilities of the paramagnetic phase (NLRO) occur. A magnetic instability takes place for $U\sim W$, the magnetic periodicity of the spin-density wave (SDW) being three times larger than the crystallographic one (as in the $\sqrt{3}\times\sqrt{3}$ structure of the usual *kagomé* lattice). Increasing V drives a charge-density-wave (CDW) state reminiscent of the insulating structure obtained in Ref. 11 by the slave-boson technique. It would be interesting to estimate parameters of the $LaCuO_{2.66}$ compound using the expression given by the RPA calculation for small U/W: $J_1\sim-0.12U^2/W$. At present we cannot do it: the bandwidth has been calculated[9] only for the Y compound ($W\sim1$ eV) and the exchange interaction ($J_1\sim20$ K) has been derived[1] considering that the magnetic moments are interacting as in a triangular lattice, but we have seen that the number of neighbors in the effective lattice is four with only $\frac{2}{3}$ magnetic ions, implying a larger J_1.

$RCuO_{2.66}$ delafossites. Now we come back to the materials that motivated this work. The resistivity ρ of the hexagonal phase of the Y compound displays variable-range hopping, behavior typical of localized states. For the La case the intrinsic ρ is probably lower.[1] The large susceptibility χ and comparable specific-heat γ enhancement of $LaCuO_{2.64}$ have been interpreted in terms of strong correlations near a metal-AF-insulator instability.[3] A two-component model describing the creation of local singlets as the temperature is lowered, as well as simultaneously accounting for the mass-enhancement of a metallic part, has been shown to fit the data. However, as remarked by the authors,[3] the applicability of this model, initially proposed for Si:P,[14] in such a different parameter system, is intriguing. A qualitative different picture emerges for $Y_{0.99}Ca_{0.01}CuO_{2.65}$. The observation of a large χ enhancement, ~5 without γ enhancement has been explained by the proximity of a ferromagnetic instability.[3]

The possibility of a Brinkman-Rice transition due to the interatomic Coulomb repulsion V has also been invoked[11] to explain these distinct behaviors. Since the hopping between Cu sites is ~16 times smaller than in superconducting cuprates, a moderate V drives a localization transition in the structure proposed for oxygen content 8/3, the La and Y compounds being on different sides of this transition. The fact that the lattice constants[3] are $a=3.6$ Å for $Y_{0.99}Ca_{0.01}CuO_{2.65}$ while $a=3.86$ Å for $LaCuO_{2.64}$ (a=Cu-Cu in-plane distance), i.e., shorter for the apparently insulating Y system, would be an indication of the soundness of this argument. The ^{63}Cu NMR data by Walstedt *et al.*[2] also show different behavior for $LaCuO_{2.64}$ and $Y_{0.99}Ca_{0.01}CuO_{2.65}$. In contrast with the La case, the spectrum of the Y compound shows that there are at least two different Cu sites in the lattice, in a 2:1 proportion, the major quantity corresponding to sites of localized magnetism. Although all these features agree with the metallic and localized phases proposed for the La and Y compounds,[11] the fact that their site symmetries appear to be trigonal or higher do not.

In conclusion, the present study shows the interesting properties of the lattice depicted in Fig. 1, indicating that this particular topology and dilution should be crucial parameters in the understanding of the puzzling magnetic behavior of $RCuO_{2.66}$ delafossites. If as suggested, the La compound is in the paramagnetic metallic phase,[11] it is certainly very close to the magnetic instability. For fixed nonmagnetic sites, as it is probably the case for R=Y, only chains are created, in-

volving infinite or six magnetic sites, depending on the magnitude of the Coulomb repulsion between Cu^{3+} sites compared to the quantum exchange energy. This could be an explanation of the lack of magnetic LRO experimentally observed down to low temperatures, but then this one-dimensional character should appear in the physical properties. Although we believe that this approach is closer to the real RCuO$_{2.66}$ compounds than previous analysis, which do not take into account the particular structure, more experimental data is required for further investigation. Particularly important would be neutron experiments allowing conclusions about the distribution of the nonmagnetic Cu^{3+} sites and the dynamics of the Cu^{2+} magnetic moments. The energy and space scale of the characteristic fluctuations will certainly indicate the relevance of the different possible scenarios that we have discussed.

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