Ordering of magnetic clusters in CuO_2 planes of 1–2–3 superconductors

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A possible ordering of magnetic clusters in the CuO_2 planes of oxide superconductors of the 1–2–3 type, which would result in the formation of ferromagnetic conducting tapes, is discussed. It is suggested that the main structural fragment is a five-nucleus copper cluster with an oxygen hole, which has a spin $S=2$ and a nonmagnetic ground state $|0\rangle$. The first excited state, $|\pm 1\rangle$, is separated from the ground state by an energy on the order of 1 K. © *1995 American Institute of Physics.*

It was shown in Ref. 1 that, at sufficiently low temperatures ($T \ll T_c$), a spin–lattice relaxation of ^{169}Tm nuclei in the superconductors $TmBa_2Cu_3O_{6+x}$ ($TmBCO_{6+x}$) occurs as the result of either paramagnetic centers or paramagnetic copper–oxygen clusters. The concentration of the paramagnetic centers, which increases as the oxygen content x is raised from 0 to 0.4, reaches its highest value at the insulator–metal transition. As x is raised further, to 1.0, this concentration falls off sharply. Comparison of the concentration of paramagnetic centers, $N_0(x)$, found from NMR experiments,[1–3] with the concentration of charge carriers (holes), $n_p(x)$, in the CuO_2 planes[4] leads to a curious conclusion (Fig. 1): The concentrations N_0 and n_p are equal at the insulator–metal transition, as if each hole in a CuO_2 plane were bound to a paramagnetic center. Later experiments[5] revealed a change in the kinetics of the restoration of the longitudinal nuclear magnetization of thulium in a $TmBCO_{6.5}$ sample at low temperatures. Specifically, the kinetics is described below 1 K by

$$1-M_t/M_\infty=\exp[-(t/T_1)^{1/2}], \tag{1}$$

which is characteristic of a random 3D distribution of paramagnetic centers in the crystal lattice.[6] At $T>2$ K, in contrast, the law which holds is

$$1-M_t/M_\infty=\exp[-(t/T_1)^{1/3}], \tag{2}$$

which corresponds to a 2D distribution of paramagnetic centers.[7] A behavior of the type in (2) clearly indicates that the paramagnetic centers formed by holes are indeed localized in CuO_2 planes neighboring Tm^{3+} ions. At the same time, a change caused in the nature of the kinetics upon deep cooling by the apparent disappearance of the paramagnetic centers of acceptors in CuO_2 planes could be explained in a natural way in terms of a redistribution of the populations of the energy levels of the paramagnetic centers. All we need to assume is that the paramagnetic centers have an integer spin $S \geqslant 1$ and a nonmagnetic ground state $|0\rangle$, separated from the nearest excited state (a magnetic state), $|\pm 1\rangle$, by an energy on the order of 1 K (Ref. 5).

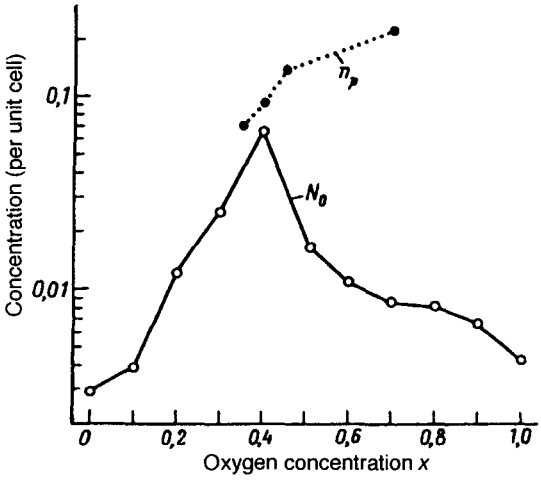

FIG. 1. Concentration of paramagnetic centers, N_0 (according to data on the NMR of ^{169}Tm in $TmBCO_{6+x}$; Refs. 1–3), and concentration of charge carriers, n_p, in the CuO_2 planes (Ref. 14; $YBCO_{6+x}$) versus the oxygen concentration in the CuO_x planes.

That paramagnetic centers, i.e., magnetic defects, would be present in the antiferromagnetic lattice of the oxygen-deficient 1–2–3 compounds is not in itself surprising, since these compounds have a disordered crystal structure. On the contrary, we would naturally expect that the diverse structural defects associated with the disorder of the oxygen sublattice would give rise to a variety of magnetic defects. Measurements of the specific heat[8] and the nuclear quadrupole resonance of Cu(1) (Ref. 9) suggest that there are also paramagnetic centers with half-integer spins $S=1/2$ and $S\geqslant 5/2$ in the $YBCO_{6+x}$ compounds. Here, however, we would like to stress that most of the paramagnetic centers are formed by holes in CuO_2 planes near the insulator–metal transition, and these centers have an integer spin and a nonmagnetic ground state. What sort of structure could they have? We regard as likely candidates paramagnetic centers with a spin $S=1$ [a hole is localized at a $Cu^{3+}(2)$ copper ion[10]] and a paramagnetic center with a spin $S=2$ (five-nucleus copper clusters;[11] Fig. 2a). The former look less probable, since the initial splitting of the energy levels of the Cu^{3+} ion is usually considerably smaller than 1 K (Ref. 12). For clusters with a spin $S=2$, on the other hand, the energy interval between the $|0\rangle$ and $|\pm 1\rangle$ levels can lie between 0.6 and 2.3 K, according to estimates.[11] Another argument (perhaps the strongest one) that $S=2$ clusters play the role of paramagnetic centers in the CuO_2 planes comes from the sharp decay of the concentration $N_0(x)$ to the right of the insulator–metal transition, i.e., at values of x between 0.4 and 0.6, as the carrier concentration in the CuO_2 planes increases (Fig. 1). According to the hypothesis of a percolation nature of the conductivity (and of the superconductivity) of the layered cuprates,[13] the behavior $N_0(x)$ and $n_p(x)$ can be explained in a natural way by assuming that the conductivity results from a stacking of "building blocks," i.e., clusters with a spin $S=2$, into tapes: At $x>0.4$, the number of isolated (paramagnetic) blocks decreases, and tapes with delocalized holes are nucleation centers of the conducting phase.

As we know, not only well-annealed $YBCO_{6+x}$ samples with $x\geqslant 0.35$, but also samples quenched in liquid nitrogen are superconductors, although in the latter case the transition temperature T_c is always lower, and it increases as time elapses if the sample is left at room temperature.[14] This effect is usually linked with an ordering of oxygen atoms

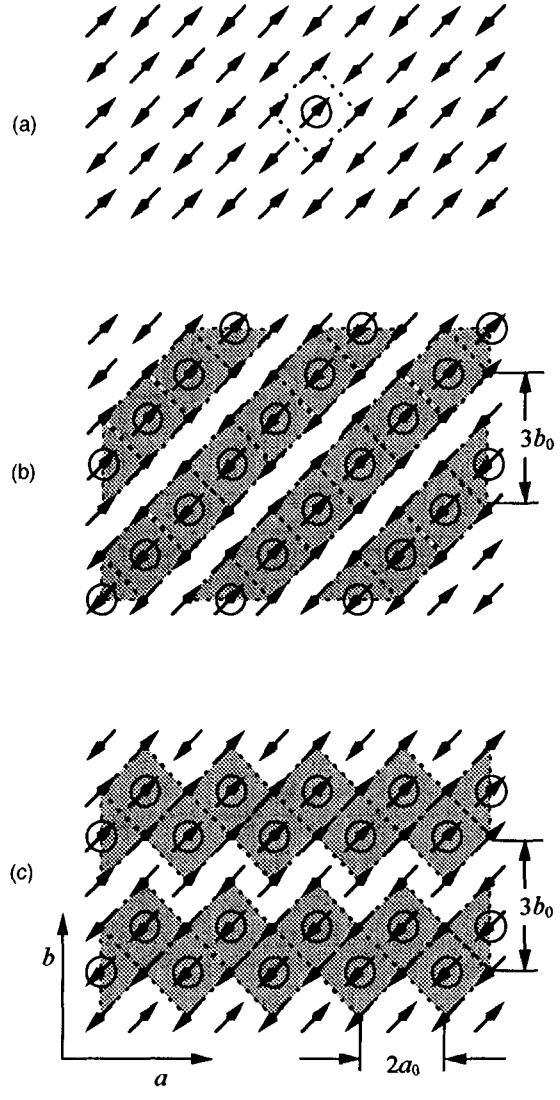

FIG. 2. a: Antiferromagnetic lattice of CuO_2 and isolated copper–oxygen cluster with spin $S=2$. The oxygen atoms are not shown. Arrows—Cu spins; arrow with circle—spin of an oxygen hole which "cancels" the copper spin. b: Ferromagnetic tapes constructed from clusters with $S=2$ in the [110] direction. c: Ferromagnetic tapes in the [100] direction.

in CuO_x planes which leads to an elongation of fragments of Cu–O–Cu chains and to an additional doping of CuO_2 planes with holes.[15] If these additional holes form new clusters with a spin $S=2$, the configuration of the percolation cluster should change. Accordingly, along with an ordering of oxygen atoms in CuO_x planes we should allow for a possible ordering of percolation clusters in CuO_2 planes. Figure 2b shows the simplest model of an ordering of this sort. This ordering resembles the model proposed in Ref. 16, but the directions of the central spins are reversed. The reason is that the exchange interaction of an oxygen hole with copper spins outweighs the superexchange interaction of copper spins. The presence of charge density waves in CuO_2 planes and thus a varia-

tion of the crystal potential at the rare-earth ions should be observable properties of the ordered model of Fig. 2b. Edwards *et al.*[17] have reported observing a corrugated surface of a cleaved $YBCO_{6+x}$ crystal by scanning tunneling microscopy at $T=20$ K (a CuO_x "chain" layer). The period of the corrugation was 13 Å, or approximately three times the lattice constant ($3b_0$). Edwards *et al.*[17] attributed the observed corrugation to charge density waves in the CuO chains, but one cannot dismiss the possibility that the CuO chains might have played the role of an indicator of charge density waves in CuO_2 planes. We know that the oxygen atoms in these CuO chains can easily be displaced from their equilibrium positions (by as much as 0.074 Å, even in a sample with a stoichiometry[18] $YBCO_{6.98}$). At any rate, the observed period of the corrugation is the same as that which would follow from the model of Fig. 2b.

With regard to spatial variations of the crystal potential associated with fluctuations of the charges O(2, 3) and Cu(2), we note that they are manifested in, for example, an asymmetry of spectral lines corresponding to inelastic scattering of neutrons by Ho^{3+} excited states in the superconductors $HoBa_2Cu_3O_7$ and $HoBa_2Cu_4O_8$ (Ref. 19). We wish to stress that this asymmetry has been observed in specifically superconducting materials, and not only in a 1–2–3 compound, but also in a 1–2–4 compound, with a perfect crystal structure. Accordingly, this asymmetry could not be related in any way to an oxygen disorder in CuO chains.

The idea of a 1D order of magnetic clusters in CuO_2 planes accompanied by the formation of conducting chains (or tapes) is not in itself new; it was first reported in Ref. 20. The primary distinguishing feature of the model of the present letter is that the main structural unit is assumed to be a five-nucleus copper cluster with an oxygen hole, which flips the central copper spin. As a result of an alignment of clusters, we obtain a ferromagnetic tape, in which displacements of holes do not require any expenditure of energy associated with flips of copper spins.

The simplest way to verify the existence of isolated clusters with a spin $S=2$ is to observe corresponding ESR signals. Since the number of single clusters falls off rapidly with increasing value of the oxygen index ($x=>0.4$), samples with $x=0.4$–0.5 should be used in ESR experiments. The results of such experiments are described in Refs. 21 and 22. In particular, the ESR spectra of a quenched $GdBCO_{6.5}$ crystal were studied. [The oxygen index here is determined from the temperature of the annealing preceding the quenching, $T=1020$ K (Ref. 22), in accordance with the relation $6+x=7.44-1.27\times10^{-3}(T^*-273)$; Ref. 23.] Putting aside a possible interpretation of the experimental data offered in Ref. 22 and analyzing only the actual results of the measurements of the ESR spectra of $GdBCO_{6.5}$ at 1.6 K, we find that these results can be described fairly well by the spin Hamiltonian

$$\mathscr{H}=g_{\parallel}\mu_B H_z S_z+g_{\perp}\mu_B(H_x S_x+H_y S_y)+D\left[S_z^2-\frac{1}{3}S(S+1)\right]$$

with $S=2$, $g_{\parallel}=2.15$, $g_{\perp}=2.0$, and $D/k=0.9$ K. Those results thus support our suggestions.

Recent studies[24] of photoelectron spectra of a $Bi_2Sr_2CaCu_2O_{8+x}$ crystal show that the CuO_2 conducting planes have a (2×2) superstructure. The shape of the ferromagnetic

tapes in Fig. 2c agrees with that observation. This configuration of the conducting tapes imposes a restriction on the "allowed" directions of the wave vectors of the charge carriers ($\mathbf{k}\|[100]$ and $\mathbf{k}\|[010]$). As a result, the energy gap of the superconducting cuprates may be anisotropic, if there is a pairing of carriers in neighboring tapes. It has been established[25] that the gap in the same Bi2212 crystal is 20 ± 5 meV for $\mathbf{k}\|[100]$ or [010], while it is 5 ± 5 meV for $\mathbf{k}\|[110]$. According to the model of Fig. 2c, these results may simply mean that the concentration of carriers with $\mathbf{k}\|[110]$ is very small (as is the density of states at the Fermi level).

Going back to the 1–2–3 system, we note that in the model of Figs. 2b and 2c, the maximum concentration of holes per Cu(2) atom, corresponding to a close packing of the conducting tapes, is 1/3. Since there are two CuO_2 planes, coupled by tunneling holes,[26,27] in a 1–2–3 compound, the maximum hole concentration turns out to be half this value (1/6), i.e., precisely the value corresponding to the optimum doping level and the maximum transition temperature.[28]

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