Characteristic features of the magnetic state of Cu–O chains in $YBa_2Cu_3O_{6.0+x}$

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The change in the state of Cu atoms in $YBa_2Cu_3O_{6.0+x}$ ($0.05 \leqslant x \leqslant 0.95$) is studied on the basis of the measurements of the magnetic susceptibility, ESR, and NQR of ^{63}Cu and the Mössbauer measurements of ^{57}Fe. The results of calculations of the magnetic interaction, in combination with all other data collected, show that magnetic moments form at CuI atoms in the oxygen-deficient chains. At $T \sim 10$ K the magnetic moments are "frozen-in" in the semiconducting region of the compositions ($x \leqslant 0.4$). The behavior of the NQR frequencies near T_c is discussed.

A change in the concentration of oxygen in some $YBa_2Cu_3O_{6+x}$ compounds causes a change in their structure and in the electric, magnetic, and superconducting properties. Because of the theory concerning the special role played by the magnetism in high-temperature superconductivity,[1] many investigators have studied the magnetic properties of these compounds. Nevertheless, the key questions concerning the nature of magnetic interactions and the possibility of forming localized magnetic moments at Cu1 and Cu2 have so far not been answered. Our goal was to study in detail the concentration behavior of the magnetic properties of copper atoms in $YBa_2Cu_3O_{6+x}$ ($0.05 \leqslant x \leqslant 0.95$) by the local methods. We saw no evidence of antiferromagnetic ordering in the Cu2–O planes, which exists near $x \approx 0$ (Refs. 2–4) and which apparently vanishes rapidly with increasing x. At the same time, the behavior of the magnetic properties of the Cu1–0 chains turned out to be unusual.

The samples were synthesized from the compound $YBa_2Cu_3O_{6.95}$ by annealing them at the temperatures and partial pressure of O_2 corresponding to the unknown x of the equilibrium P_0–T–x diagram.The values of x given below correspond to the data of the thermogravimetric analysis.[5] The methods of fabrication, measurement, and calculation are described in Ref. 6. For the Mössbauer studies we replaced Cu by 0.5% ^{57}Fe, which was added to the initial composition in the form $Fe(NO_3)_3$ to insure a uniform distribution of the atoms. The distribution uniformity was monitored by a microscopic x-ray structural analysis.

The magnetic susceptibility χ was measured at $4.2\ K < T < 450$ K. Near the normal state, $70\ K < T < 300$ K, the following equation describes the behavior of the susceptibility satisfactorily: $\chi = \chi_0 + C/(T\text{-}\Theta)$. At $x < 0.6$, χ was found to increase slightly, as in Refs. 7 and 8, as the temperature was raised above 300 K. This increase

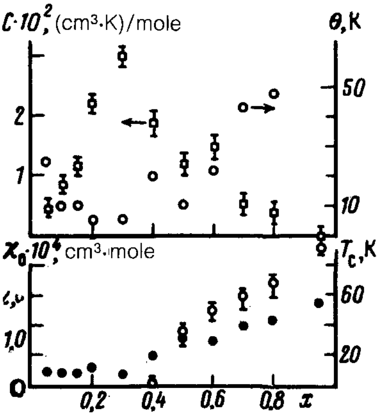

FIG. 1. Concentration dependence of C, θ, χ_0, and T_c determined from the measurements of the magnetic susceptibility.

seems to be linked with the particular features of the band structure near E_{ph}. It can be seen from the concentration dependences of χ_0, C, Θ, and T_c, determined in the ac measurement of χ (Fig. 1), that (a) the localized magnetic moment component depends nonmonotonically on x and is at a maximum at $x = 0.3$, μ_{eff} $(x = 0.3) = 0.4$ μ_{B}/unit cell and (b) $\Theta > 0$, suggesting that there is a ferromagnetic short-range order. Whether the localized magnetic moment forms at Cu1 or at Cu2 can apparently be determined directly by using the Mössbauer method. At $T = 300$ K the Mössbauer spectrum of ^{57}Fe has a hyperfine structure which shows that there is a super-position of three quadrupole doublets: the outer doublet D_1 corresponds to the displacement of the Cu2 positions, the intermediate doublet D_2 corresponds to the displacement of the Cu1 positions, and the slightly split, low-intensity doublet apparently corresponds to the defective position with an oxygen environment, which is similar to the octahedral environment. This interpretation is based on the fact that the ratio of the areas of the outer doublet and the intermediate doublet is 2.0 ± 0.1. It can be seen from the distribution of the quadrupole splitting QS, which is reconstructed from the Mössbauer spectra, that as the temperature is lowered to 77 K, doublet D_1 remains nearly constant, while D_2 becomes strongly diffuse. The deposition of doublet D_1 on the outer wing at $x = 0.2$ (Fig. 2c) corresponds to the splitting of D_2, as can be seen from the analysis of the areas of the spectral lines. It can thus be assumed that the localized magnetic moment forms at a Cu1 atom and that the splitting of the D_2 lines as the temperature is lowered is a Zeeman splitting which is caused by the appearance of a magnetic order (in general, a short-range order). These conclusions have been confirmed by the nuclear quadrupole resonance spectra[6] of ^{63}Cu and ^{65}Cu.

The conclusive argument in favor of the localized magnetic moment is the observation of the ESR signal at $0.1 \leqslant x \leqslant 0.3$. The lineshape and the value of the g-factor allow us to conclude that it belongs to Cu^{2+}. As can be seen from Fig 3, at $x = 0.3$ the linewidth ΔH decreases linearly with decreasing T in the temperature region 15 K $< T <$ 50 K, which is apparently attributable to the phonon relaxation mechanism. In the temperature region 10 K $< T <$ 15 K the behavior of ΔH changes dramatically. The g-factor and ΔH increase with further lowering of the temperature, suggesting

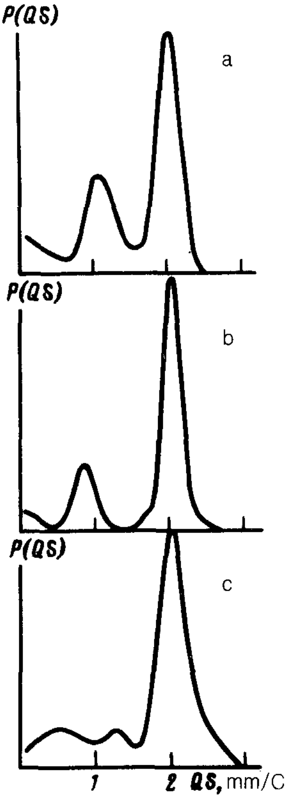

FIG. 2. Distribution of the quadrupole splittings, reconstructed from the Mössbauer spectra of $YBa_2Cu_{2.995}Fe_{0.015}O_{6.0+x}$. (a) $x = 0.95$, $T = 300$ K; (b) $x = 0.2$, $T = 300$ K; (c) $x = 0.2$, $T = 77$ K.

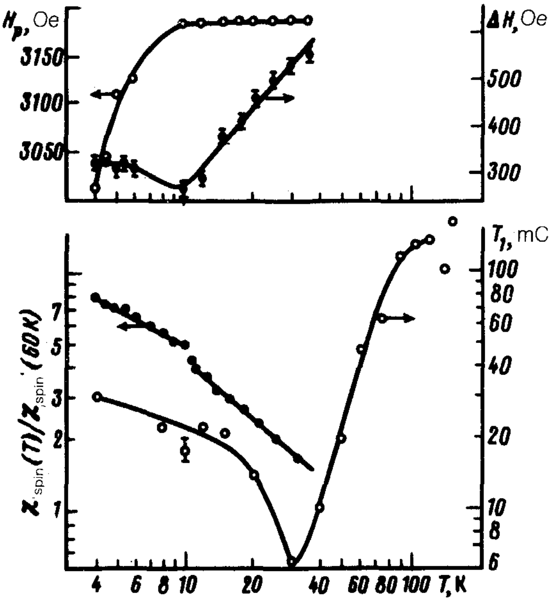

FIG. 3. Temperature dependence of the position H_p and width ΔH of the ESR line, of the spin susceptibility χ_s, and of the spin-lattice relaxation time T_1 of ^{63}Cu positions of Cu2 ($\nu_Q = 30.2$ MHz) for $x = 3$.

that there is a magnetic phase transition at $x = 0.3$ and $T \approx 10$ K. At these temperatures we also see that the spin-lattice relaxation time $T_1(T)$ of ^{63}Cu atoms in the Cu2 positions ($\nu_Q = 30.2$ MHz) is minimum[6] (Fig. 3). This minimum indicates that the frequency of the spin fluctuations decreases sharply, $\tau^{-1} \approx \omega_Q$; i.e., the electron spins in the chains freeze-in. In the temperature region 15 K $< T <$ 50 K the spin susceptibility determined from the ESR, $\chi_{\rm spin}$, is described satisfactorily by the law $\chi_{\rm spin} \approx T^{-0.8}$, which is characteristic of quasi-one-dimensional magnets.[9]

The localized magnetic moments detected in Cu1 may be related to the Cu1a position (two neighboring oxygen atoms in the O_4 positions), to the Cu1b position (one oxygen atom and one vacancy) or to the Cu1c position (two vacancies). The nature of the ferromagnetic short-range order also remains unclear. To solve these problems, we calculated the nonlocal magnetic suceptibility

$$\chi_{ij} = \frac{1}{\pi} \operatorname{Im} \sum_{LL'} \int^{E_\Phi} dE\, G^{ij}_{LL'}(E)\, G^{ji}_{L'L}(E).$$

Here the Green's function was found from the LMTO of the band-theory calculations of $YBa_2Cu_3O_7$ by integrating over the Brillouin zone, ij are the node indices, and L is the orbital state. According to the criterion for the existence of localized magnetic moments[10]: $I\chi_{00} \geqslant 1$ (I is the Stoner exchange parameter), at $x = 1$ the localized magnetic moments are absent. We found $I\chi_{00} = 0.14$ for Cu1 and 0.2 for Cu2. According to Szpuner *et al.*,[4] at $x = 0$ Cu1 also has no localized magnetic moments. For $0 < x < 1$ the localized magnetic moments are thus apparently related to the Cu1b positions, in qualitative agreement with the fact that $C(x)$ is maximum at $x = 0.3$ (Fig. 1) and also in qualitative agreement with the concentration and temperature evolutions of the width and the relative intensity of the nuclear quadrupole resonance lines at the frequencies $\nu_Q = 22$ MHz (Cu1a), 24 MHz (Cu1c), and 30 MHz (Cu2) (Ref. 6).

The results of the calculations of χ_{ij} and $J_{ij} = I^2\chi_{ij}$ for the adjacent atoms are given in Table I. In the case of the appearance of localized magnetic moments J_{ij} have the significance of the exchange interaction parameters. The results of calculations show that the exchange in the planes is of an antiferromagnetic nature and the exchange in the chains is of a ferromagnetic nature if the Cu1–Cu2 coupling is weak.

TABLE I. Exchange interactions of copper-copper atoms.

	χ_{ij}, Ry^{-1}	J_{ij}, K
Cu2 – Cu2	−0.051	−40
Cu1 – Cu1	0.072	+56
Cu2 – Cu1	−0.010	−7

Since the chain-adjacent chain exchange coupling is absent ($|J| \ll 1$ K), a Cu–O–Cu superexchange in fact takes place.

Such a description of the magnetism of the Cu–O chains apparently explains the fractional power law $\chi_{\rm spin}(T)$. For $0 < x < 1$ the chains are comprised of fragments ...–Cu–O–Cu... of length l, which are divided by vacancies and the superexchange of the localized magnetic moments at the fragment ends decreases exponentially with increasing l. In the case of a Poisson distribution, $p(l) \sim \exp(-l(1-x))$, the usual line of reasoning[9] would then lead to a fractional power-law asymptotic behavior of the distribution of $p(J)$ in the limit $J \rightarrow 0$ and hence to the dependence $\chi_{\rm spin} \sim T^{-(1-\alpha)}$ ($\alpha \ll 1$).

The nuclear quadrupole resonance frequencies ν_Q show that near T_c there are very sharp anomalies (on the order of several percent) in $YBa_2Cu_3O_7$ (Ref. 11) and in $La_{2-x}Ba_xCuO_4$ (Ref. 12) which are attributable, in our view, to the screening near T_c. It has been established that in the leading order in T_c/E the polarization term $\pi(\mathbf{q},0)$, which determines the screening of the longitudinal nonuniform electromagnetic field with the wave vector $\mathbf{q}$, remains constant in the transition to the superconducting state.[13] It can be shown, however, that corrections to $\pi(\mathbf{q},0)$ due to superconducting pairing characterized by the gap Δ are moderately small and are singular in the limit $T \rightarrow T_c$ ($\Delta \rightarrow 0$). Calculations of $\pi = \Sigma_{\mathbf{q}} \pi(\mathbf{q},0)$ on the basis of the BSC model gives $\delta\pi = 2N(E_{\rm ph}) \times \Delta(T) \ln(T_c/E_{\rm ph}) \sim \sqrt{T_c - T}$, where $N(E_{\rm ph})$ is the electronic state density of the normal phase. The anomalies found in Refs. 11 and 12 may thus be the result of a relatively large value of $N(E_{\rm ph})\,\Delta$ in the high-T_c superconductors. At $x < 1$ we did not observe any anomalies in ν_Q near T_c apparently because of the diffuse transition and because of the sharp decrease of $N(E_{\rm ph}) \sim \chi_0$ (Fig. 1) and Δ (Ref. 14) as x is reduced. The anomalies in the thermal expansion and in the elastic moduli at T_c are similar in nature[15,16] since $\delta\pi$ determines the scale of these anomalies in the phonon spectra and in the corresponding contributions to the thermodynamic properties.

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