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Paramagnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$ at high temperatures

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The magnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$ for different oxygen concentrations is measured up to temperatures of 1000 K. In the semiconducting concentration range $\delta > 0.5$, the susceptibility exhibits the typical behavior of a two-dimensional Heisenberg antiferromagnet. For the exchange interactions Cu(2)-Cu(2) and Cu(1)-Cu(1) we estimate $J = 1000$ and 3000 K, respectively. The concentration dependence of the paramagnetic susceptibility at the semiconductor-superconductor phase boundary provides indications for the existence of antiferromagnetic fluctuations in the superconductors.

The superconducting pairing mechanism is the central problem for the perovskite-type high-temperature superconductors. Magnetic pairing models have been proposed,[1-4] but the detailed mechanism is far from being solved. The magnetic pairing models predict the existence of strong magnetic correlations in the superconducting state. Indications for the existence of these fluctuations have been found in light scattering experiments,[5,6] direct evidence from neutron scattering experiments is still lacking.

The magnetic order which exists in the semiconducting state of $(La_xSr_{1-x})_2CuO_4$ and $YBa_2Cu_3O_{7-\delta}$ (Refs. 7-9) supports the assumption of a magnetic coupling mechanism. The insulating compound $YBa_2Cu_3O_6$ has the highest Néel temperature of these compounds with $T_N \simeq 420$ K, the magnetic structure is a simple antiferromagnetic lattice of the Cu(2) $s = \frac{1}{2}$ spins with nearest-neighbor antiferromagnetic alignment in one Cu(2) plane and between two subsequent Cu(2) planes. The Cu(1) ions in $YBa_2Cu_3O_6$ are in the valence state 1+ and thus are nonmagnetic.[8,9]

The crystallographic layer structure and the nearly isotropic orbital singlet ground state of Cu^{2+} makes $YBa_2Cu_3O_6$ a quasi-two-dimensional Heisenberg antiferromagnet, which can develop magnetic long-range order only due to weak magnetic coupling between the layers.

As we will show below, the measured susceptibility of the samples in the semiconducting range of $YBa_2Cu_3O_{7-\delta}$ is consistent with two-dimensional Heisenberg antiferromagnetism. Since the Néel temperatures are above room temperature, it is essential to extend the susceptibility measurements to high temperatures. Susceptibility measurements below room temperature, numerous examples of which exist in the literature, are not very informative, since the intrinsic susceptibility of the antiferromagnet is often completely masked by susceptibility contributions from paramagnetic impurity phases.

The measurements we will show in the following have been done on one single polycrystalline sample with the starting composition $YBa_2Cu_3O_{6.9}$. The sample was prepared following the standard procedure; it was single phase by x-ray analysis and had a superconducting transition at 92 K with a resistive width of 1 K. The Meissner effect measured in a field of 10 Oe was 60% of the ideal diamagnetic value; the demagnetizing field was corrected for the calculation of this value.

The magnetic susceptibility was measured by a Faraday balance with a temperature range from 2 to 1000 K in an applied field of 1 T. An important advantage of the Faraday technique is the fact that the oxygen content of the sample can be varied and controlled *in situ* by using the balance with the magnetic field switched off as a sensitive thermogravimetric apparatus.

For a measurement of the sample $YBa_2Cu_3O_{7-\delta}$ with a certain oxygen stoichiometry the sample was heated up to an annealing temperature above 400 °C in the vacuum of the Faraday balance. After reaching oxygen equilibrium, which typically takes 0.5 h, the sample is quenched to room temperature and the susceptibility is measured during slowly heating up of the sample. The maximum temperature for a measurement at a certain oxygen content is set by the beginning of additional oxygen loss.

The results of the measurements of the sample at six different oxygen concentrations are given in Fig. 1.

The susceptibility increases continuously with the oxygen content at high temperatures, the semiconducting

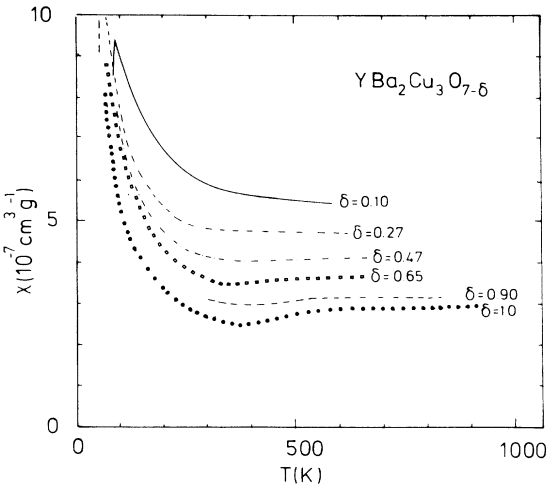

FIG. 1. Magnetic susceptibility as a function of temperature for $YBa_2Cu_3O_{7-\delta}$ samples.

samples ($\delta > 0.5$) exhibit a definite minimum of the susceptibility for temperatures above room temperature, and the susceptibility has a positive temperature gradient for these samples above the minimum.

Below room temperature, the susceptibility increases strongly until the onset of superconductivity; this increase is known to originate from impurity phases containing paramagnetic Cu^{2+} ions.[10,11] At low temperatures, the term from the paramagnetic impurities dominates and the total measured susceptibility approximately follows a Curie-Weiss law (Fig. 2). The Curie-Weiss term turns out to be independent of the oxygen stoichiometry and corresponds to about 3 at.% of the Cu ions in a paramagnetic Cu^{2+} state.

The intrinsic susceptibility of pure $YBa_2Cu_3O_{7-\delta}$ can be derived by subtracting the paramagnetic contribution as given by the straight line in Fig. 2. There is some ambiguity in the definition of the Curie-Weiss term, but the intrinsic susceptibility above room temperature which is used for a calculation of the exchange constants below, is insensitive to the choice of slightly different Curie-Weiss terms.

The intrinsic susceptibility for samples $YBa_2Cu_3O_{7-\delta}$ now shows the characteristic feature of two-dimensional Heisenberg antiferromagnets (Fig. 3).[12] For two-dimensional (2D) Heisenberg antiferromagnets it is known that the Néel temperature correlates with the maximum slope of the parallel susceptibility in single crystals.[12] For polycrystalline samples T_N is difficult to derive from $\chi(T)$ measurements exactly, but it correlates approximately with the kink in the susceptibility as indicated by the arrows in Fig. 3. The Néel temperatures thus derived are in reasonable agreement with those determined from neutron scattering experiments.[8,9]

The characteristic feature of 2D Heisenberg antiferromagnets is a maximum in the paramagnetic susceptibility at temperatures far above T_N. The temperature of the maximum in χ is determined by the value of the exchange interactions within the 2D layers, from high-temperature

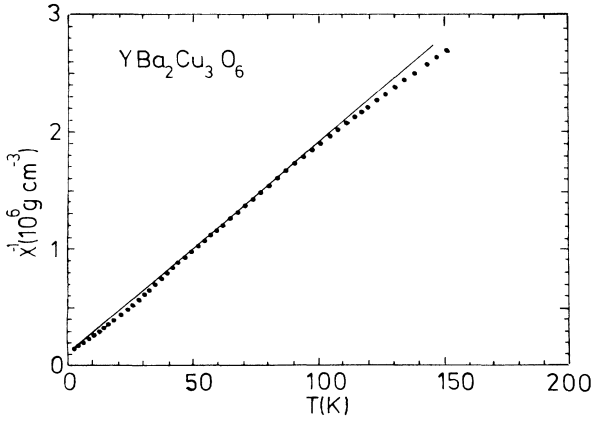

FIG. 2. Reciprocal magnetic susceptibility as a function of temperature for the sample $YBa_2Cu_3O_6$. The drawn line gives the approximation of the susceptibility due to the paramagnetic impurities we have used to derive the intrinsic susceptibility of $YBa_2Cu_3O_{7-\delta}$.

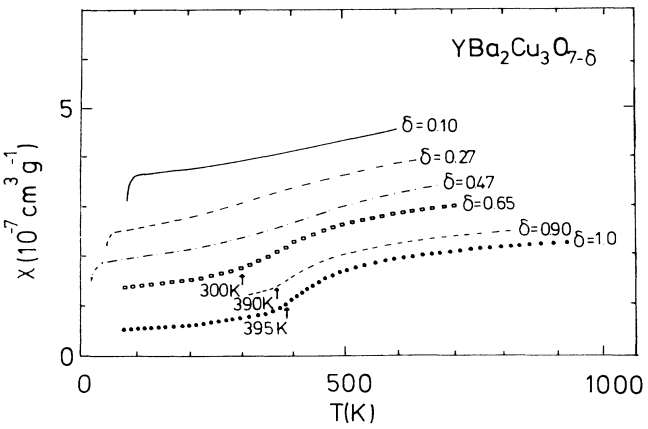

FIG. 3. Intrinsic magnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$ as function of temperature; the arrows indicate the Néel temperatures.

series development calculations of a quadratic 2D Heisenberg antiferromagnet one expects $T_{max} = 2.55JS(S+1)$ (intralayer exchange J, spin quantum number S).[13]

In Fig. 3, one finds that T_{max} is not yet reached at the highest experimental temperature $T = 960$ K for the sample $YBa_2Cu_3O_6$. This gives $J_2 > 500$ K for the antiferromagnetic exchange J_2 in the Cu(2) planes. Comparing the slope $d\chi/dT$ at 960 K with the 2D model systems in Ref. 12 one estimates $T_{max} \geq 2000$ K; from this follows $J_2 \geq 1000$ K, consistent with $J_2 = 1360$ K derived from the Brillouin-scattering experiments.[6]

Principally, the antiferromagnetic in-plane exchange interaction can be calculated precisely by fitting the experimental $\chi(T)$ curves with the high-temperature series development results. But in the present case this turns out to be difficult. The measured susceptibility is the sum of three contributions of the same order of magnitude namely $\chi = \chi_{AF} + \chi_{dia} + \chi_{vv}$ (antiferromagnetic susceptibility χ_{AF}, core diamagnetism χ_{dia}, and the van Vleck contribution χ_{vv} from the mixing of higher crystal-field orbital states of Cu^{2+}). $\chi_{dia} = 2.9 \times 10^{-7}$ cm^3/g can be calculated from standard tables, but χ_{vv} depends on the crystal-field splitting of the orbital levels of the Cu^{2+} ions. For a cubic crystal field one can calculate $\chi_{vv} = 4N\mu_B^2/10Dq$ (Ref. 14) (when Dq is the crystal-field parameter and standard notation is used for the other symbols). We adopt this formula and approximate the tetragonal crystal field for the Cu^{2+} ions by a cubic crystal field with a total splitting $10Dq$ of 1.2 eV, estimated from the crystal-field splitting in the optical spectra of Ref. 15. One then derives $\chi_{vv} = 3.1 \times 10^{-7}$ cm^3/g and $\chi_{AF} = 2 \times 10^{-7}$ cm^3/g at $T = 960$ K. Assuming further that χ_{AF} will increase up to T_{max} by 10%, which is not very critical, since $\chi(T)$ is very flat below the maximum in 2D Heisenberg $s = \frac{1}{2}$ antiferromagnets, we derive $J_2 = 1050$ K by using the formula from[12] $\chi(T_{max}) = 0.045Ng^2\mu_B^2/J_2$ (Landée factor $g = 2$ and the standard notation for the other symbols). The largest uncertainty in this calculation comes from the rough estimation of χ_{vv}, which in reality may differ from the value given above by about $\pm 20\%$ giving a similar error bar for J_2.

For the other two samples in the semiconducting concentration range ($\delta=0.9$ and $\delta=0.65$) the susceptibility in Fig. 3 retains the typical temperature dependence of a 2D antiferromagnet. For these samples, a part of the Cu(1) atoms have a magnetic moment and, thus, contribute to the paramagnetic susceptibility. The system then becomes more three dimensional, since the Cu(1) moments couple the magnetic Cu(2) layers by the superexchange interaction J_3 between Cu(1) and Cu(2). But J_3 is expected to be weak and ferromagnetic,[16] thus, the two layered-spin systems Cu(1) and Cu(2) are expected to be weakly coupled. This has been observed in recent neutron scattering experiments on $YBa_2Cu_3O_{6.35}$ (Ref. 9) showing that the Cu(1) spins order at 40 K only and then disturb the magnetic structure of the Cu(2) spins slightly.

Neglecting the weak coupling J_3 and assuming that the exchange interaction J_2 does not change with the oxygen concentration in the semiconducting range, one can attribute the difference $\Delta\chi$ of the semiconducting sample and the sample with $\delta=1$ directly to the Cu(1) spins. Using the same formula as above one estimates $J_1\simeq 3000$ K for the exchange interaction between the Cu(1) spins. This value seems to be very high, but one should note that the assumption of two independent spin systems Cu(1) and Cu(2) for the calculation of the susceptibility is rather crude.

We now discuss the susceptibility of the superconducting samples in Fig. 3. The kink in the susceptibility indicating the onset of magnetic long-range order is absent, but the temperature dependence of the susceptibility at high temperatures is very similar to that observed for the semiconducting samples, strongly suggesting that antiferromagnetic short-range order develops at high temperatures in the superconducting samples too.

The experimentally observed continuous behavior of the concentration dependence of the susceptibility at the metal-semiconductor transition (Fig. 4) supports the following conclusion.

If one assumes that for the superconductors the antiferromagnetic fluctuations (and the local Cu moments) do not exist, the measured susceptibility would be of purely Pauli type. One would then expect a changeover of the character of the susceptibility from purely spin-fluctuation type to purely Pauli type close to metal-semiconductor phase boundary $\delta=0.5$. The vanishing susceptibility from spin fluctuations and the low number of charge carriers then should lead to a dip in the measured susceptibility close to $\delta=0.5$, as indicated by the dash-dotted line in Fig. 4. This is difficult to reconcile with the experimental results.

On the other hand, assuming that the antiferromagnetic fluctuations continue to exist in the superconducting phase and contribute the dominant part of the susceptibility, the continuous behavior of $\chi(\delta)$ at the metal-semiconductor phase boundary finds a natural explanation. A quantitative separation of the susceptibility from the antiferromagnetic fluctuations and the Pauli susceptibility χ_P, is a delicate problem, since the charge carriers (essentially holes in the oxygen p bands) are expected to modify J_1 and J_2.[4] In Ref. 4 arguments are given that the effective antiferromagnetic exchange J_2 and J_1 should decrease with the number of charge carriers; correspondingly, the susceptibility contribution from the antiferromagnetic fluctuations should increase in the superconducting concentration range, as drawn schematically by the dashed line in Fig. 4.

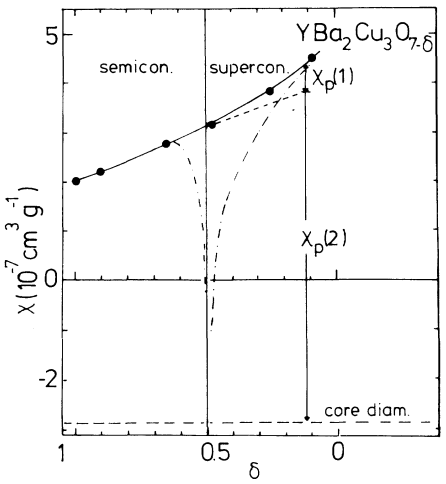

FIG. 4. Intrinsic magnetic susceptibility of $YBa_2Cu_3O_{7-\delta}$ from Fig. 3 at 600 K as function of the oxygen content. $\chi_P(1)$ and $\chi_P(2)$ denote the Pauli susceptibility derived when assuming that antiferromagnetic fluctuations do exist [$\chi_P(1)$] or do not exist [$\chi_P(2)$] in the superconducting concentration range. (For the explanation of the drawn lines see main text).

The dashed line cannot be given quantitatively; thus, the Pauli susceptibility, too, cannot by given exactly in this case. An estimation for the upper limit of χ_P can be derived by assuming that the spin fluctuation part of the susceptibility remains unchanged in the superconducting concentration range (corresponding to a horizontal dashed line in Fig. 4). One then gets $\chi_p=1.3\times10^{-7}$ cm^3/g for the 90-K superconductor $YBa_2Cu_3O_{6.9}$, this value is a factor of five lower than χ_P resulting when the antiferromagnetic fluctuations are neglected.

In summary, we have shown that the susceptibility at high temperatures for the semiconducting samples in $YBa_2Cu_3O_{7-\delta}$ exhibits the typical temperature dependence of a 2D Heisenberg antiferromagnet. The temperature dependence and the concentration dependence of the susceptibility in the superconducting concentration range point strongly towards the existence of antiferromagnetic fluctuations in the high-temperature superconductors.

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