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Evidence for an interplay between superconductivity and antiferromagnetism of rare-earth ions in $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$

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Here, we report on ac susceptibility measurements which reveal an anomaly associated with antiferromagnetic ordering of Gd^{3+} ions at $T_N = 2.45$ K in the fully oxygenated superconducting $Gd_{1.2}Ba_{1.8}Cu_3O_{7.03}$ with the critical temperature $T_c = 42$ K. This anomaly is explained as a result of the enhanced pair-breaking effect near the magnetic phase transition. This is the first evidence, to our knowledge, that in the high-T_c copper oxides of the Y123-type superconductivity and antiferromagnetic ordering interact in a deep superconducting state ($T_N \ll T_c$). No signature of the interaction between conduction electrons and localized magnetic moments is observed for the $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ compositions with $x \leqslant 0.1$, i.e., $T_c \geqslant 66$ K, where superconductivity is strong and masks the effects of magnetic ordering.

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Magnetic superconductors have recently attracted growing interest with discovery of the ferromagnetically ordered state coexisting with superconductivity in UGe_2,[1] $ZrZn_2$,[2] and URhGe.[3] In these compounds, we believe that the coexistence is possible if some kind of subtle separation between magnetic and conduction electrons is present irrespective of a considered spin-triplet pairing.[3] Thus, it is important to study the interplay between magnetism and superconductivity in the case where the coupling between these subsystems is weak. This requirement seems to be fulfilled for high-temperature superconductors of the $YBa_2Cu_3O_{7-\delta}$ (Y123) type, where no significant changes of the superconducting transition temperature T_c have been observed by substituting Y with magnetic rare-earth (RE) ions.[4] A weak coupling between magnetic and conduction electrons is also required to explain the coexistence of superconductivity and long-range antiferromagnetic (AFM) ordering at low temperatures (e.g., $T_N = 2.24$ K for RE = Gd).[5] A weak but non-negligible interaction between RE $4f$ and Cu $3d$ electrons, possibly via modified oxygen $2p$ orbitals, has been verified through specific-heat and inelastic magnetic scattering measurements.[6] It remains to be shown whether or not the interaction between the localized $4f$ electrons and the conduction $3d$-$2p$ electrons of the CuO_2 planes in RE123 compounds can be revealed and studied by magnetic or transport experiments.

In the context of the multiple pair-breaking theory, the interaction between superconducting electrons and ordered magnetic moments is usually examined by analyzing an anomalous decrease of the upper critical field B_{c2} in the vicinity of the AFM ordering temperature T_N.[7] In RE123 high-T_c superconductors, B_{c2} is too large to be studied at temperatures where the long-range AFM order of the RE ions appears. However, the interaction between superconductivity and antiferromagnetism may still be observed as an AFM peak at T_N in the ac susceptibility when superconducting screening is weak such as for classic $REMo_6S_8$ and recently discovered low-T_c $RENi_2B_2C$ AFM superconductors.[7,8] To our knowledge, no such anomaly has been observed for the RE123 compounds in a deep superconducting state, i.e., at temperatures much below T_c. On the other hand, unequivocal proof of the interaction between conduction and magnetic electrons was reported from resistance measurements for ultrathin, granular $DyBa_2Cu_3O_{7-\delta}$ films with T_c reduced to a value close to T_N.[9] Additional evidence comes from the upper critical field measurements for $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ (Ref. 10)—a compound from the class of low-T_c copper oxides. For the superconducting Gd123, information pertaining to the AFM transition of Gd^{3+} ions has been obtained from neutron scattering[11] and specific-heat[5] experiments. These data have revealed $T_N \simeq 2.2$ K for both superconducting and oxygen-deficient nonsuperconducting compounds in zero applied magnetic field B.

In this paper, we report on the firm evidence that long-range AFM and superconducting orderings interact in $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ with $x = 0.2$.[12] For the $Gd_{1.2}Ba_{1.8}Cu_3O_{7.03}$ sample, T_c is decreased to 42 K and T_N is increased to 2.45 K by substitution of Gd on the Ba site while keeping the oxygen content as large as possible. For this sample, superconducting currents are unable to screen the AFM fluctuations of the Gd^{3+} magnetic moments, and as a consequence, a peak in the temperature dependence of the ac susceptibility is observed at T_N. This proves that the coupling between the localized Gd $4f$ and the conduction Cu $3d$ and/or oxygen $2p$ electrons is sufficiently strong and results in the pair-breaking effect due to the spin-disorder scattering. No signature of the AFM ordering at T_N is observed for the ac susceptibility measurements of the samples with $x \leqslant 0.1$ ($T_c \geqslant 66$ K).

Samples of $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ were synthesized resulting in superconductors with T_c decreasing from 93 to 0 K (with a plateau at 40 K) and T_N changing from 2.24 to 2.26 K (with a maximum at 2.45 K) for x varying from 0 to 0.4, respectively. In the first step, the samples were prepared in the form of a very fine powder by the citrate pyrolysis process.[13] Then, the powder was calcined in air at 900 °C for 12 h, pressed into pellets, and sintered at 940 °C for 24 h.[14] The final heat treatment was performed for 24 h at 400 °C in oxygen and at 700 °C in Ar to obtain superconducting and

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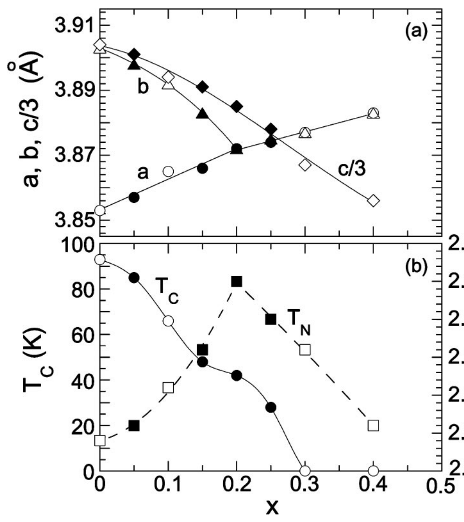

FIG. 1. (a) Lattice parameters and (b) the superconducting transition temperature T_c and the antiferromagnetic ordering temperature T_N vs composition x for oxygen annealed $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$. Open symbols represent results taken from Ref. 15.

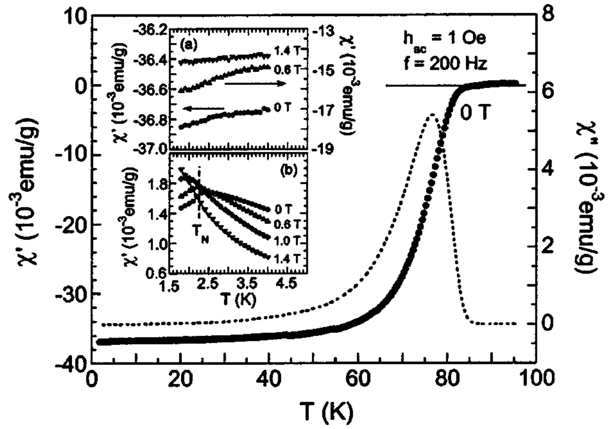

FIG. 2. Real χ' and imaginary χ'' parts of the ac susceptibility for the oxygen annealed $Gd_{1.05}Ba_{1.95}Cu_3O_{6.94}$ sample measured at zero applied field. The inset (a) shows $\chi'(T)$ for the same sample in the vicinity of T_N at $B=0$,0.6, and 1.4 T. The inset (b) shows $\chi'(T)$ for the Ar-annealed (non-superconducting) sample at $B=0$, 0.6, 1.0, and 1.4 T.

non-superconducting samples, respectively. Sample phase composition and lattice parameters were determined by x-ray powder diffraction using a Rigaku Inc. x-ray diffractometer. Sample chemical composition and homogeneity were examined using a Hitachi scanning electron microscope equipped with an energy-dispersive x-ray analyzer. Oxygen content was determined by an iodometric method and/or thermogravimetric analysis measurements using a Cahn TG171 system with slow (0.6°/min) heating and cooling rates. Susceptibility and resistivity measurements were performed in the temperature range from 1.8 to 100 K at an applied dc field B from 0 to 7 T with a Quantum Design physical properties measurement system. The susceptibility was studied upon heating from zero-field-cooled state (ZFC mode) and occasionally upon cooling (FC mode) using an ac filed $h_{ac}=1$ Oe at a frequency $f=200$ Hz. T_c was determined by resistivity measurements. T_N was determined by specific heat (in zero B) and ac susceptibility experiments.

First, the samples were carefully characterized to learn of the solubility limit for the Gd^{3+} substitution and to determine the highest T_N possible for a single-phase composition. Figure 1 presents variation of the lattice parameters and variation of T_c and T_N as a function of x for $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ with oxygen content maximized to 6.94, 6.99, 7.03, and 6.98 for $x=0.05$, 0.15, 0.20, and 0.25, respectively. Results obtained for the samples with $x=0$, 0.1, 0.3, and 0.4 are taken from Ref. 15. The existence of a single-phase solid solution extends to $x=0.4$, similar to that observed for the corresponding $RE_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ systems with RE = Sm or Nd.[16] Smaller substitution ($x=0.11$) has been achieved for $Sm_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ single crystals.[17] This indicates that, currently, only the polycrystalline materials can be synthesized with markedly increased T_N, and therefore with notably enhanced magnetic interactions. Thus, only the polycrystalline materials are available as materials suitable for our experiment. The $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ solid solution has maximum $T_N=2.45$ K for $x=0.2$. Close to this level of substitution, a transition from the superconducting orthorhombic to the superconducting tetragonal phase appears, and a plateau for the $T_c(x)$ dependence is observed at $T_c\simeq45$ K. In the tetragonal phase, T_N decreases with increasing x, most probably because of the disturbed distribution of the Gd ions for x extending above 0.2. Samples with $x=0.05$ ($T_c=85$ K, $T_N=2.26$ K) and $x=0.2$ ($T_c=42$ K, $T_N=2.45$ K) were selected for study in this work.

To ensure that we deal with bulk effects, the effective superconducting volume fraction v of the grains was estimated from the ac susceptibility measurements performed in the temperature range from 1.8 K to T_c. The appropriate correction for the grain demagnetizing effect was included, and the amount of the superconducting phase $v=30\%$ and 45% was computed for the $x=0.05$ and 0.2 samples, respectively. The estimation of v was performed at $B=7$ and 0.2 T for the $x=0.05$ and 0.2 samples, respectively, to make the grains magnetically decoupled at higher temperatures. For both samples, the shielding effect was also estimated and found to be nearly perfect at 4 K and $B=0$ ($\chi'\simeq-1/4\pi$ emu/cm^3 Oe). All of these results confirm bulk superconductivity and attest to the good quality of our specimens.[18]

The $Gd_{1.05}Ba_{1.95}Cu_3O_{6.94}$ ($x=0.05$) sample was chosen to show typical ac susceptibility results for the high-T_c AFM superconductors in the vicinity of T_N. Figure 2 shows the real χ' and imaginary χ'' parts of the ac susceptibility obtained with increasing temperature for the ZFC mode. At zero dc applied magnetic field, a sharp transition to the bulk superconducting state appears at $T_c=85$ K. The inset (a) of Fig. 2 shows $\chi'(T)$ curves for the $x=0.05$ sample at low temperatures for $B=0$, 0.6, and 1.4 T. No signature of any anomaly is observed at $T_N=2.26$ K. This is expected when the interior of the sample (interior of the individual grains) is shielded by superconducting persistent currents and the ex-

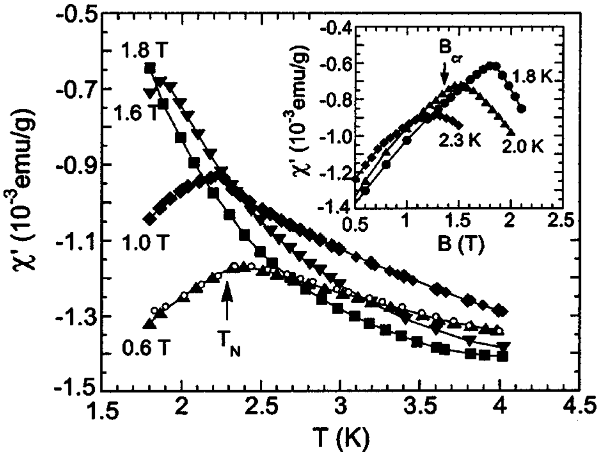

FIG. 3. Low-temperature part of the ac susceptibility χ' for the oxygen annealed $Gd_{1.2}Ba_{1.8}Cu_3O_{7.03}$ sample measured at an applied dc field $B = 0.6$, 1.0, 1.6, and 1.8 T. Open symbols represent results obtained upon cooling. The inset shows χ' measured as a function of B at constant temperatures.

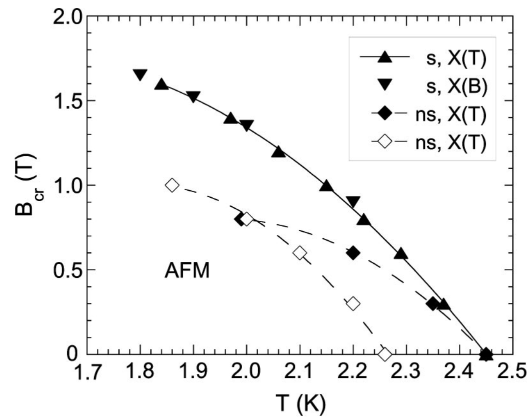

FIG. 4. Critical magnetic field B_{cr} as a function of temperature for the $Gd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ superconducting (s, triangles, solid line) and Ar-annealed non-superconducting (ns, diamonds, broken lines) samples with $x = 0.05$ (open symbols) and 0.2 (solid symbols). $X(T)$ and $X(B)$ represent results obtained from the ac susceptibility χ' measured as a function of T and B, respectively. The lines are guides for eye only.

isting transition to the AFM state is fully masked. Evidence of the magnetic transition in the $Gd_{1.05}Ba_{1.95}Cu_3O_{6.94}$ sample is a narrow peak at T_N observable in specific-heat measurements. Moreover, ac susceptibility has been measured for the $x = 0.05$ sample, which has been annealed in Ar atmosphere to destroy superconductivity. The $\chi'(T)$ results for this sample are shown in the inset (b) of Fig. 2. A clear drop is observed at $T_N = 2.26$ K for $B = 0$. The ordering temperature decreases with increasing B, as expected for AFM materials.

Clear evidence that the superconducting and magnetic subsystems can interact in the RE123 compounds is provided by the ac susceptibility measurements for the $Gd_{1.2}Ba_{1.8}Cu_3O_{7.03}$ ($x = 0.2$) sample. Figure 3 shows the low-temperature part of χ' obtained for the $x = 0.2$ sample at several dc applied magnetic fields. A significant drop in the temperature dependence of $\chi'(T)$ is observed below T_N, indicating a transition to the AFM state. The effect of increasing magnetic field is to shift T_N to lower temperatures. At fields above 1.6 T, the transition to the AFM state falls below 1.8 K, the lowest temperature available in our experiment. The inset of Fig. 3 shows χ' measured as a function of B at several T. Here, B_{cr} is a critical field for which the AFM state disappears.

The pronounced peaks that are observed close to T_N in the $\chi'(T)$ measurements of the $x = 0.2$ sample can be explained as a result of the enhanced spin-disorder scattering effect, which is due to a transition to the AFM state. In the pair-breaking approach,[19] these peaks reflect the temperature behavior of the pair-breaking parameter ρ that in a quasistatic approach is $\rho = (3J^2/\pi)\Sigma\Phi(\vec{q})\chi(\vec{q})$, where J is the exchange constant for the interaction between conduction electrons and the localized Gd^{3+} magnetic moments. The quantity $\Phi(\vec{q})$ is the joint density of states for the conduction electrons and $\chi(\vec{q})$ is the wave-vector-dependent susceptibility. For the case of q near the Fermi momentum ($q \approx k_F$), $\chi(\vec{q})$ is the main temperature-dependent component of the pair-breaking parameter. As temperature decreases towards T_N, $\chi(\vec{q})$ is expected to peak for wave vector $\vec{q} = \vec{G}$, where $\vec{G}$ is the wave vector of the ordered AFM state. This requires nesting of the Fermi surface and such a nesting may result in a resistance different from zero, which is usually observed for low-T_c AFM superconductors in the vicinity of T_N at appropriately high applied magnetic fields.[7,20]. This "reentrant" resistance is accompanied by a peak in the ac susceptibility as a function of temperature.[7,21]. For high-T_c superconductors, $G > 2k_F$ and a broad peak in ρ is expected with a maximum slightly above T_N.[19] This behavior in ρ requires a peak in the ac susceptibility, as stated above. This prediction is fully confirmed by our results, where a humplike feature in $\chi'(T)$ is observed just above T_N. For the $x = 0.2$ sample, the exchange-scattering effect is too weak to result in a resistance different from zero, so it can be observed as a magnetic effect only.

The main issue is to prove that the interaction between magnetic and superconducting subsystems is present in the sample where no separation of the magnetic and superconducting phases appears. For that reason, a B_{cr}-T phase diagram has been derived from $\chi'(T)$ measured at various B and from $\chi'(B)$ measured at various T. Figure 4 shows the B_{cr}-T phase diagram obtained for both the superconducting and the Ar-annealed non-superconducting samples with $x = 0.2$. A pronounced difference between the two $B_{cr}(T)$ dependencies is observed at higher magnetic fields. This observation, in association with the single peak of every $\chi'(T)$ curve, provides important evidence that the superconducting sample with $x = 0.2$ is free of a noticeable amount of the oxygen-deficient non-superconducting phase. Thus, this peak is interpreted as a result of the interaction between the coexisting AFM and superconducting orders. For comparison, the $B_{cr}(T)$ curve for the Ar-annealed nonsuperconducting sample with $x = 0.05$ is also shown in Fig. 4.

In conclusion, we have demonstrated that in the high-T_c copper oxides of the RE123 type, the AFM ordering of the rare-earth ions affects superconductivity in a deep superconducting state. For the $Gd_{1.2}Ba_{1.8}Cu_3O_{7.03}$ compound with $T_c = 42$ K, a clear peak in the real part of the ac susceptibility has been observed at $T_N = 2.45$ K and interpreted as a result of the conventional pair-breaking effect enhanced close to the magnetic phase transition temperature. For the $Gd_{1.2}Ba_{1.8}Cu_3O_{7.03}$ compound in a magnetic field, T_N is remarkably different for the superconducting and the oxygen-deficient non-superconducting sample. This observation, together with the single anomaly in the temperature dependence of the real part of the ac susceptibility near T_N, gives strong evidence that separation of the superconducting and the normal magnetic phases can be excluded. Thus, superconductivity and long-range AFM ordering interact here as truly coexisting effects.

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