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Influence of magnetic rare-earth ion substitution on the magnetic susceptibility of high-T_c superconductors

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We report detailed magnetic-susceptibility studies for the oxygen-deficient perovskite superconductors $M\mathrm{Ba_2Cu_3O_{7-\delta}}$ (M = Y,Gd,Er,Ho). Normal-state behavior above T_c shows weak ferromagnetic (antiferromagnetic) tendencies for M = Y,Gd (M = Er,Ho), with 87% of the free-ion moment for M = Gd,Er,Ho. The estimated Fermi-level density of states is 6.4 states/eV Cu for M = Y,Gd, which is twice the band-structure estimate. The superconducting state shows a 20% or more flux exclusion at small field. The Curie contributions for M = Gd,Er,Ho are weakened for $T < T_c$ due to diamagnetic screening. The local moments appear to have little or no effect on the superconducting state. These effects are well described by a simple theoretical model.

The insensitivity of T_c to the substitution of magnetic rare-earth ions in oxygen-deficient perovskite superconductors raises important questions about the relationship between superconductivity and magnetism in these systems. In particular, studies of the resistive transition in single-phase ceramic superconductors of the class $M\mathrm{Ba_2Cu_3O_{7-\delta}}$, where M = Y, Gd, Er, or Ho, show $T_c \simeq 90$ K, despite the existence of large magnetic moments for Gd, Er, and Ho.[1-4]

In this report, we present detailed measurements of the magnetic susceptibility for the above series of oxide superconductors. Our measurements above T_c confirm observations that the susceptibility obeys a Curie-Weiss law,[5] with the Curie constant scaling accurately with the effective moment for the isolated rare-earth ions. Our measurements below T_c show clearly that the Curie susceptibility is basically unchanged by the superconducting transition, provided that the reduction in the local magnetic field by diamagnetic screening in the superconducting grains is properly allowed for. We also present a straightforward but relatively accurate model of this screening that characterizes the porous, polycrystalline ceramic as a composite of voids and superconducting grains. The model successfully identifies two distinct regions in the low-temperature ($T < T_c$) susceptibility, each characterized by the parameter $R/\lambda(T)$, where R is the superconducting grain size and $\lambda(T)$ is the penetration depth.

In order to achieve chemically homogeneous materials, samples were prepared using the coprecipitation technique. Stoichiometric mixtures of M, Ba, and Cu nitrate were first dissolved and then slowly precipitated with the addition of sodium carbonate. The resulting power precipitate was dried overnight at 140 °C and then fired at 900 °C for 6 h in air. The sample was then pulverized and rebaked at 900 °C several times, finally yielding a black powder that was pressed into pellet form and sintered for 12 h at temperatures ranging from 850 to 950 °C. The pellet was then annealed in 1 atm of O_2 at 500 °C, and cooled in O_2 over several hours to room temperature.

Samples were characterized by measurements of the temperature dependence of the resistive transition and by room-temperature x-ray powder diffraction scans. X-ray diffraction studies (not shown) of all of our "1-2-3" compounds show clearly that the orthorhombic perovskite structure[6-8] is obtained by our sample preparation method. Furthermore, the absence of lines associated with secondary phases establishes that the susceptibility measurements are truly associated with a single phase. Table I summarizes the lattice constants for all samples as inferred from the x-ray data.

Magnetic-susceptibility measurements were performed in a variable-temperature cryostat on polycrystalline pellet samples using a Faraday technique[9] in external magnetic fields up to 7 T. Sample temperatures were varied from 300 to 2 K. The reported susceptibility is the ratio of the magnetization to the applied field, normalized to specific units by the sample mass.

To emphasize the differences between M = Y and M = Gd,Er,Ho, we have plotted in Fig. 1 the temperature-dependent dc magnetic susceptibility $\chi(T)$ of all our

TABLE I. Lattice parameters for $M\mathrm{Ba_2Cu_3O_{7-\delta}}$. The values for M = Y are from Ref. 8.

M	a	b	c
Y	3.8231	3.8864	11.6807
Gd	3.8415	3.8954	11.6842
Er	3.8152	3.8822	11.6502
Ho	3.8253	3.8856	11.6578

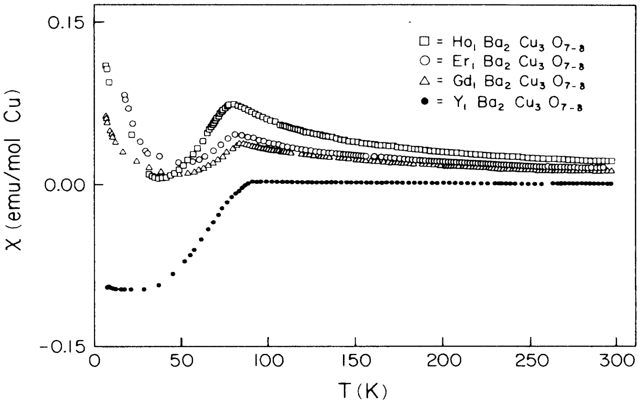

FIG. 1. Magnetic susceptibility for $M\mathrm{Ba_2Cu_3O_{7-\delta}}$ (M = Y, Gd, Er, and Ho) at a field of 2.17 kG.

$M\mathrm{Ba_2Cu_3O_{7-\delta}}$ samples in the relatively high applied field of 2.17 kG. As reported earlier,[10] the magnetic susceptibility of the Y compound becomes diamagnetic below T_c. In contrast, the compounds with a magnetic rare-earth ion show only a decrease in $\chi(T)$ relative to the normal-state behavior, without becoming negative. The low-temperature upturn is then attributed to the rare-earth local moments, but is not a simple extrapolation of the high-temperature Curie-law behavior. In lower fields, a true diamagnetic susceptibility is seen for all compounds, as we shall discuss later.

For the temperatures above T_c, $\chi(T)$ has been fitted to the form $\chi=\chi_0+\chi_c(T)$, where $\chi_c(T)=C/(T-\Theta)$, χ_0 is the sum of core diamagnetic, Pauli, and Van Vleck contributions, C is a constant, and Θ is the Curie-Weiss temperature. Plotted in Fig. 2 is a fit of the above formula for the M=Er compound. The parameters for the four different compounds are summarized in Table II.

The inset in Fig. 2 is a plot of the measured Curie constant C versus the calculated effective moment for the rare-earth ions [$p^2=g_J^2J(J+1)$, where J is the Hund's-rule ground-state angular momentum]. The linear relationship shows that the rare-earth moments are systematically smaller than the expected value by a factor of 0.87. We offer three possible explanations for this result. First, the nitrates used in the coprecipitation are highly hydroscopic, containing sizable amounts of water which can lead to deviations of order 5% in the assumed stoichiometry, and similar deviations in the value of C. However, the errors induced by this problem are more likely to be random (and of either sign) than systematic. The second possibility is that crystal-field effects give rise to an effective temperature-dependent, reduced Curie constant for the Er and Ho samples. However, this leaves the

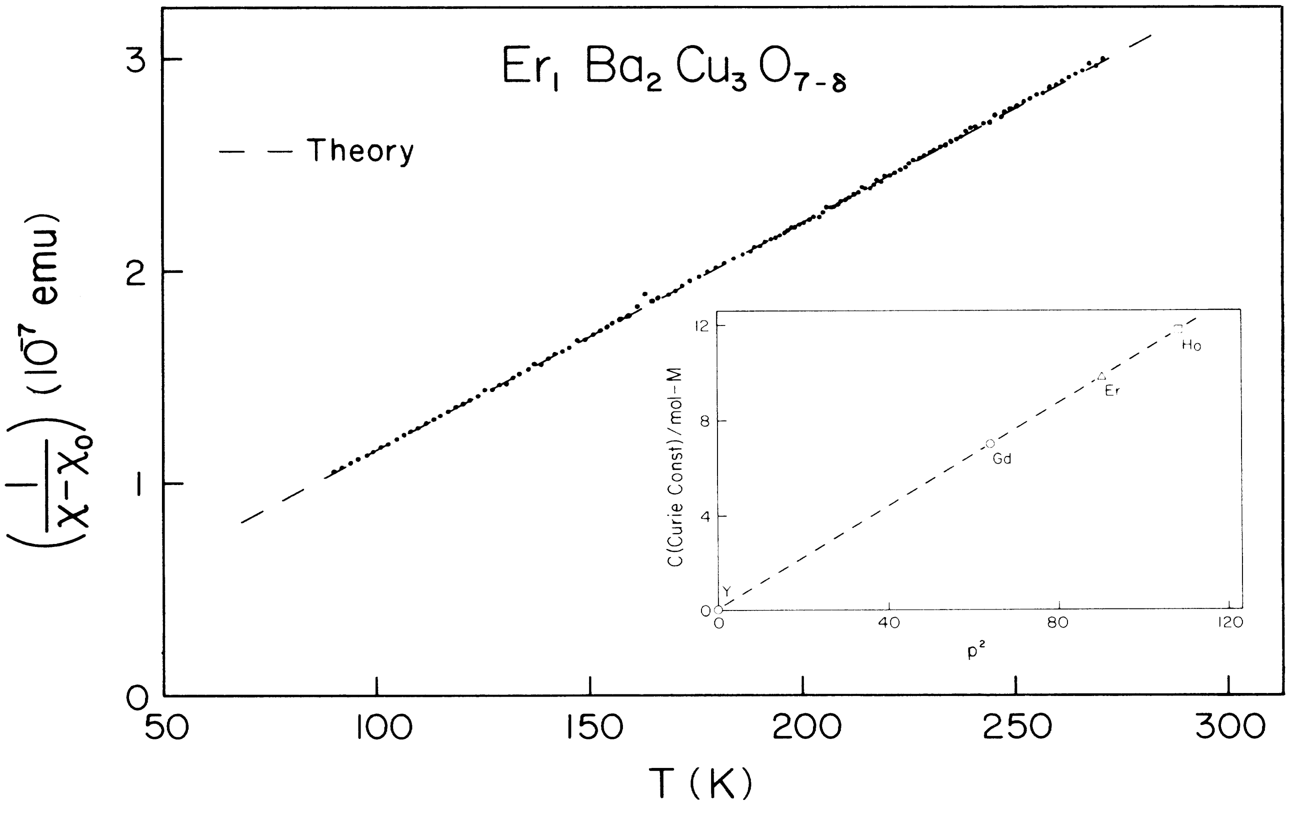

FIG. 2. Curie-Weiss fit of the form $\chi=\chi_0+C/(T-\Theta)$ for $\mathrm{ErBa_2Cu_3O_{7-\delta}}$ at high temperature. The inset is the Curie constant vs p^2 where $p^2=g_J^2J(J+1)$.

TABLE II. Normal-state susceptibility fitting parameters. The assumed form is $\chi(T) = \chi_0 + C/(T - \Theta)$.

M	χ_0/mol M	Θ,K	C/mol M
Y	$5.58e-04$	+20.0	$4.51e-02$
Gd	$5.80e-04$	+3.0	7.13
Er	$5.35e-03$	−8.0	9.81
Ho	$3.35e-03$	−7.8	11.8

Gd result unaccounted for. A third possibility is that some intrinsic diamagnetic shielding (of unknown origin, but well above the level of core diamagnetism) persists in these samples at high temperatures.

An alternate fitting procedure for the normal-state susceptibility is possible, taking C as fixed by the free-ion moment and χ_0 as fixed by the result for the single-phase M=Y based sample. This overestimates the data and also leads to the conclusion that an unexplained temperature-dependent diamagnetic contribution is present.

We can obtain an estimate for the Fermi-level density of states $[N(E_F)]$ from the constant susceptibility term χ_0, once we subtract Van Vleck and core diamagnetic corrections. For M=Y,Gd, the Van Vleck contributions are negligible (Gd having a pure spin moment). The diamagnetic contributions are taken as $-12, -32, -15, -12\times10^{-6}$ emu/mole for Y,Ba,Cu,O respectively.[11] The remaining constant term was assigned to the Pauli susceptibility, with $\chi^{\text{Pauli}} = \mu_B^2 N(E_F)$. This yields $N(E_F) = 6.4$ states/eV Cu for M=Y,Gd, which is to be compared with 3 states/eV Cu obtained from electronic structure calculations.[12] This discrepancy could be due to Stoner enhancement of the susceptibility since the Coulomb correlation energies for these materials are expected to be rather high.

The constant susceptibility terms found for M=Er,Ho are much larger than estimated atomic Van Vleck[13] values using known spectroscopic splitting[14] of the spin-orbit multiplets. The large χ_0 values might be related to crystal-field splittings of the Er and Ho ions. Recent neutron scattering experiments indicate a large (order 80 meV) total crystal-field splitting in the Er compound,[15] while calorimetric measurements yield estimates of the lowest crystal-field splittings of 90 and 8 K for M=Er and M=Ho, respectively.[16] Using the measured average transition matrix element $[\frac{1}{3}\sum_{i=x,y,z}\langle J_i\rangle^2 = 17.6$ (Ref. 15)] and the 90-K minimum splitting for M=Er gives a zero-temperature crystal-field-induced Van Vleck contribution of 0.1 emu/mole. Since this contribution rolls off above the 90-K splitting, it is not at all inconceivable that crystal-field-induced Van Vleck contributions of the order of 5×10^{-3} emu/mole exist at room temperature. Given past experience with magnetic superconductors, the presence of a Curie-law fit in a polycrystalline sample despite large crystal-field splittings is possible, though counterintuitive.[17]

The derived Curie temperatures (Θ) suggest weak ferromagnetic tendencies for M=Y,Gd, and weak antiferromagnetic tendencies for M=Er, Ho, although these results may not be directly related to the character of any eventual low-temperature magnetic transitions. The inter-ion coupling deduced from Θ for M=Gd is small compared with that of Gd metal and may well correspond to in-plane ferromagnetic correlations. The observed three-dimensional ordering for M=Gd is apparently antiferromagnetic, with calorimetric measurements yielding $T_N \simeq 2.2$ K.[18] For M=Er, antiferromagnetic order has been observed at $T_N = 0.63$ K, while no ordering has yet been observed for the Ho-based material.[19]

The Curie law observed for M=Y is likely due to a small concentration of a secondary phase. Previous measurements on a multiphase sample gave a C value corresponding to about 0.5 ($S=\frac{1}{2}$) moments per Cu atom,[10,20] but in our well-characterized single-phase sample that number has gone down by an order of magnitude. Similar single-phase results have been reported elsewhere.[21]

The susceptibility for M=Er,Y between 4 and 100 K as a function of magnetic field (between 100 and 2000 G) is plotted in Figs. 3(a) and 3(b). As can be seen, the slope of the susceptibility near the superconducting transition is very sharp at H=117 G. At this low field, the susceptibility decreases from a relatively small paramagnetic value to an almost constant negative value as temperature is decreases from 87 to about 60 K. For M=Er, the low field susceptibility starts curving upward at about 20 K, which is a manifestation of the Er magnetic moments. The total

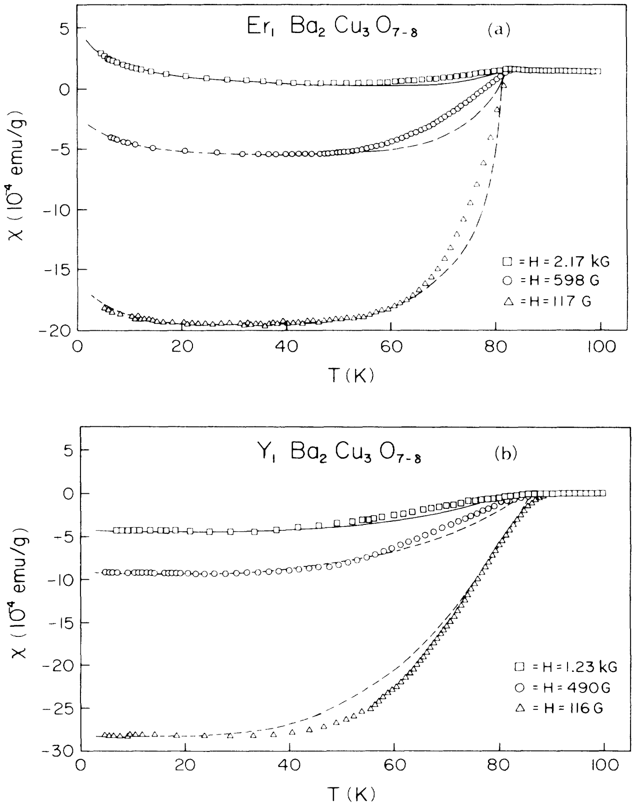

FIG. 3. Magnetic susceptibilities for (a) $ErBa_2Cu_3O_{7-\delta}$ and (b) $YBa_2Cu_3O_{7-\delta}$ in different fields at low temperature. The dashed lines are fits using Eq. (1).

flux exclusion at this field is estimated to be about 20% of the full Meissner-effect result.

Strong field dependence of the susceptibility is observed. As the magnetic field increases, the fully developed diamagnetic response is reduced, the temperature range over which χ decreases from paramagnetic behavior at T_c to a flat diamagnetic region is much broader, and for $M=\mathrm{Er}$, the low-temperature upturn is enhanced relative to the diamagnetic plateau. Note that for $M=\mathrm{Er}$, the susceptibility never goes to a negative value at the relatively high field of $H=2.17$ kG. We propose that this is a consequence of the domination of the reduced diamagnetism by the remnant paramagnetic tail of the Er ions. The $M=\mathrm{Ho}$ sample shows the same field dependence, while for $M=\mathrm{Gd}$ the crossover in temperature to a diamagnetic plateau is broader. Note that in contrast to the magnetic ion-based samples, for $M=\mathrm{Y}$ the susceptibility below T_c never goes positive in fields up to $H=6$ kG and has almost no remnant Curie tail at the lowest temperature.

The dashed lines in Fig. 3 are theoretical fits obtained by assuming the rare-earth spins do not interact with the superconducting electrons, and respond to the internal magnetic field with the normal-state Curie-law susceptibility $\chi_c(T)$ determined from our fits to the data above T_c. Since the internal field includes the diamagnetic screening of the superconducting electrons, the measured paramagnetic response of the rare-earth moments is reduced. Because the samples are multiply connected porous composites and strongly type II in character, the diamagnetic contribution $\chi_d(T)$ to the measured susceptibility is reduced by a field-dependent fraction $f(H)$, where H is the applied magnetic field. Thus, our equation for the measured susceptibility is

$$\chi(T,H)=\chi_0+\chi_c(T)[1+4\pi\chi_d(T)]+f(H)\chi_d(T) \ . \qquad (1)$$

We neglect any changes in the Pauli susceptibility through the transition, as that will be small compared to either the superconducting or local moment contributions.

As a simple model, we assume the polycrystalline single-phase material consists of spherical grains of radius R whose susceptibility depends on the ratio of R to the penetration depth $\lambda(T)$.[22] A value of $R/\lambda(0)=2$ for Y and 10 for Er is used, consistent with the known values of the grain size from scanning electron microscopy analysis and estimates of the penetration depth from the carrier density.[21] The behavior of $f(H)$, determined by a fit of the data to Eq. (1) for each value of field, shows a strong decrease with increasing H. This is qualitatively consistent with a type-II-like penetration of flux into the sample.

The deviation of the fits near T_c is consistent with the polycrystalline nature of the samples and a distribution of grain sizes. Near T_{nc} where $\lambda(T)$ diverges, $\chi_d(T) \simeq -\langle R^2\rangle/60\pi\lambda^2(T)$, where $\langle R^2\rangle$ is the mean-square grain radius, while far below T_c the penetration depth is expected to be small compared to the typical grain size so that $\chi(T)\simeq-[1-3\lambda(T)\langle 1/R\rangle]/4\pi$, with $\langle 1/R\rangle$ the mean of the inverse radius. Thus, near T_c the mean value of R^2 is relevant, while far below T_c, the mean value of $1/R$ is relevant, and the susceptibility shows a crossover between these two regimes, which improves agreement with experiment.

Our data and the success of our simple model provide clear evidence that there is little interaction between the rare-earth moments and the superconducting electrons. This is consistent with the notion that the superconductivity is quasi two-dimensional and strongly confined to the Cu-O planes above and below the M site. However, it is conceivable that in fields sufficiently high to polarize the rare-earth moments the resulting strong internal field might inhibit the superconductivity and reduce the upper critical field. Further work is required to test this idea.

In summary, we have made detailed measurements of the magnetic susceptibility on the oxygen-deficient perovskite superconductors $M\mathrm{Ba_2Cu_3O_{7-\delta}}$ with $M=\mathrm{Y,Gd,Ho,Er}$. A good fit to the normal-state data may be obtained by the sum of a Curie law and temperature-independent susceptibility. The Curie constant for each magnetic ion is 87% of the expected value which may reflect intrinsic diamagnetic shielding of an unknown origin. The temperature-independent susceptibilities for $M=\mathrm{Y,Gd}$ may be interpreted as a sum of core diamagnetism and Pauli paramagnetism, the latter yielding an estimate of 6.4 states/eV Cu for the Fermi-level density of states. The temperature-independent susceptibilities for $M=\mathrm{Ho,Er}$ are anomalously large, but may reflect large crystal-field splittings of the Hund's-rules multiplets. The Curie-law fits suggest weak antiferromagnetic tendencies for $M=\mathrm{Er,Ho}$ and weak ferromagnetic tendencies for $M=\mathrm{Y,Gd}$. The small Curie tail for $M=\mathrm{Y}$ is likely due to a secondary phase. In the superconducting state we have successfully modeled the susceptibility as a sum of contributions from diamagnetically screened local moments which do not interact with the superconducting electrons and the diamagnetic response of a porous, polycrystalline type-II superconductor. Our results quantitatively support the idea that the rare-earth moments have little or no effect on the superconducting state due to the confinement of the relevant electrons to the Cu-O layers above and below the M sites.

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