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Electronic, steric, and dilution effects on the magnetic properties of $Sm_{2-x}M_xCuO_{4-y}$ ($M=$Ce, Y, La, and Sr): Implications for magnetic pair breaking

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Recent data suggest that the high-T_c compound $Sm_{2-x}Ce_xCuO_{4-y}$ presents considerable difficulties for conventional theories of magnetic pair breaking. We report results of x-ray diffraction, superconducting-quantum-interference-device magnetization, and resistivity measurements for single-phased polycrystalline specimens of $Sm_{2-x}M_xCuO_{4-y}$ ($M=$Ce, Y, La, and Sr) for various x and y. In each case, the magnetic Sm^{3+} ions are diluted by a nonmagnetic species: isovalent Y^{3+} and La^{3+}, or nonisovalent Ce^{4+} and Sr^{2+}. Rare-earth magnetic order occurs below 6 K in Sm_2CuO_4; isovalent dilution with $M=$Y results in a depression of the Néel temperature T_N at an initial rate $(1/T_{N0})(dT_N/dx)=-0.0110/\text{at.}\,\%$, a result that can be well described by a simple theory of magnetic dilution. Isovalent dilution with $M=$La reveals a small steric effect. Nonisovalent dilutions are interpreted in terms of concentration-dependent exchange interactions; electron and hole dopings result in depression and enhancement of the rare-earth exchange coupling, respectively. Our results ($\mathcal{J} \lesssim 6$ meV) indicate that the coupling between rare-earth ions and superconducting electrons is probably much smaller than previously suggested, and that conventional magnetic pair-breaking theory adequately describes these materials. Some magnetic features suggestive of a subtle transition in the range $x=0.10$–0.15 in the insulating $M=$Ce series are also observed.

I. INTRODUCTION

The discoveries of high-temperature superconductivity in the $L_{2-x}Ce_xCuO_{4-y}$ ($L=$Pr, Nd, Sm, and Eu; $x \approx 0.15$),[1,2] and $L_{2-x}Th_xCuO_{4-y}$ ($L=$Pr, Nd, and Sm; $x \approx 0.15$),[2–4] compounds and, more recently, in the infinite-layer $Sr_{1-x}Nd_xCuO_2$ material[5] have demonstrated that superconductivity can occur by electron doping into an insulating copper-oxide parent compound. Such materials, with relatively modest T_c's (3–42 K), offer the opportunity to access a greater portion of their phase diagram with attainable laboratory magnetic fields. Recently, an upper-critical-field investigation[6] of the magnetic superconductor $Sm_{2-x}Ce_xCuO_{4-y}$ provided evidence that an appreciable interaction between rare-earth magnetic order and superconductivity can exist in the copper oxides. As discussed below, such strong interactions would indicate that the high-T_c materials present considerable difficulties for conventional theories of magnetic pair breaking. We present measurements here that attempt to quantify rare-earth–conduction-electron interactions by a comparative magnetic dilution technique. We find that while electron (or hole) doping causes considerable changes in Sm-Sm exchange couplings, little, if any, additional indirect exchange coupling via conduction electrons can be deduced. The result suggests that the rare-earth–conduction-electron exchange interactions are much smaller than previously suggested, and that conventional pair-breaking theory at present adequately accommodates magnetic interactions in these materials.

After a discussion of experimental details in Sec. II, some theoretical remarks and preliminaries concerning both magnetic pair-breaking and magnetic dilution appear in Sec. III. Experimental results, discussion, and analysis are presented in Sec. IV, followed by summarizing remarks in Sec. V.

II. EXPERIMENTAL

Polycrystalline specimens of $Sm_{2-x}M_xCuO_{4-y}$ ($M=$La, Y, Sr, and Ce) were prepared by solid state reaction from stoichiometric mixtures of high-purity oxides or carbonates: 99.99% Sm_2O_3, Y_2O_3, CeO_2, La_2O_3, $SrCO_3$, and 99.999% CuO. Samples were sintered in air at 900 °C for ten days, with several intermediate grindings, then compressed into pellets under ~2 kbar pressure, and fired in air at 1100 °C for three days; a buffer layer of the same material was used to avoid contamination from the alumina crucibles. Samples were then annealed in flowing oxygen, cooling from 900 °C at the rate of 25 °C/h. All iodometric titrations performed on such oxygen-annealed specimens of $Sm_{2-x}M_xCuO_{4-y}$ indicated oxygen deficiencies $y=0.00\pm0.02$; all such specimens will subsequently be termed $Sm_{2-x}M_xCuO_4$. For $M=$Ce, oxygen annealing may actually result in excess oxygen content ($y<0.00$), as recently suggested;[7] however, such differences could not be detected within our accuracy ($\Delta y \approx 0.02$). To induce metallic and/or superconducting behavior in the $M=$Ce specimens, a reduction anneal in flowing He was performed: The samples were heated at 2 °C/min to 850 °C, annealed for 16 h, and rapidly cooled to room temperature over a period of 0.5 h. For $M=$Ce, both oxygenated and reduced samples were studied. Titrations of reduced specimens indicated oxygen deficiencies $y=0.02\pm0.02$.

Phase purity and lattice constants were determined by x-ray powder diffraction using a Phillips 42273 diffractometer, Cu $K\alpha$ radiation, and internal silicon standards. A nonlinear least-squares fit of the eleven intense peaks occurring in the range $2\theta=20°-60°$ was used to determine lattice constants. With the exception of the $x=0.20$ specimen for $M=\mathrm{Ce}$, which exhibited a trace impurity ($\sim 1\%$ unreacted $\mathrm{CeO_2}$), all samples for which magnetic, structural, or transport data are reported below were single phased. A comparison with the $M=\mathrm{Ce}$ superconducting system is the main intent of this study; the tetragonal T' phase persists[1-3] in the polycrystalline $\mathrm{Nd_{2-x}Ce_xCuO_4}$ system only for concentrations up to $x\approx 0.20$. (For flux-based single-crystal growth of $\mathrm{Nd_{2-x}Ce_xCuO_4}$, the solubility range apparently extends[8] up to $x\approx 0.23$; for polycrystalline $\mathrm{Sm_{2-x}Ce_xCuO_4}$, the limit[9,10] may be only $x\approx 0.18$.) Thus the $M=\mathrm{La}$, Y, and Sr systems were studied in detail only over the concentration range $x=0-0.20$. We note, however, that the $M=\mathrm{La}$ and Y systems were observed to be single phased over broader ranges, up to $x\approx 1.0$ and 0.5, respectively. For $M=\mathrm{Sr}$, however, a narrower range of dopant solubility occurs: impurity peaks were observed for all specimens with $x\geq 0.15$; a plot of the intensity of such impurity peaks versus concentration extrapolates to zero intensity at $x\approx 0.10$. Thus, for $M=\mathrm{Sr}$, only data for $x=0.05$ and 0.10 specimens are reported here.

Magnetic data were obtained using a Quantum Design Model MPMS SQUID magnetometer. Typically, a magnetic field $H=1000$ Oe was applied; for several specimens, measurements at higher and lower fields indicated that the reported data represent low-field (field-independent) susceptibilities. Corrections ($\sim 2\%$) for the susceptibility of the sample capsules were made. Néel temperatures were determined from the cusp in the magnetic susceptibility by identifying the temperature at which extrapolations of the data above and below the cusp intersected. Other magnetic parameters were determined by nonlinear least-squares fitting of the full temperature dependence of the susceptibility as described below. For resistivity measurements, platinum wires were attached to gold contact pads on $\sim 1\times 1\times 6$ mm^3 bar-shaped specimens using silver epoxy; data were obtained using a Linear Research LR-400 four-wire bridge operating at a frequency of 17 Hz.

III. THEORETICAL CONSIDERATIONS

In this section, we first review relevant aspects of magnetic pair breaking in superconductors, including recent results for $\mathrm{Sm_{2-x}Ce_xCuO_{4-y}}$. The exchange coupling between the superconducting electrons and the rare-earth ions will be denoted $\mathcal{J}$. We comment on the behavior of T_c in the $L_{2-x}M_x\mathrm{CuO}_{4-y}$ system and the expected effects of magnetism on superconductivity. We then turn our attention to antiferromagnetism; the net exchange coupling between two rare-earth ions is denoted $\mathscr{J}$, and the effects of dilution on the Néel temperature T_N are discussed. By accounting for the effects of isovalent dilution with constant $\mathscr{J}$, the concentration dependence of $\mathscr{J}$ due to electron doping or hole doping can be determined. Finally, the possible changes in $\mathscr{J}$ due to an additional indirect exchange enabled by the insulator-metal transition for $M=\mathrm{Ce}$ are discussed.

We consider only the simplest aspects of the interaction of magnetism with superconductivity; more comprehensive reviews may be found elsewhere.[11] Superconductivity and long-range magnetic order have been observed to coexist in many copper-oxide superconductors,[12] and the relatively low T_c of the electron-doped 2:1:4 compounds ($T_c\leq 24$ K) provides the opportunity to access much of the magnetic phase diagram with available laboratory magnetic fields. Recent upper critical field measurements[6] suggest that the exchange coupling between rare-earth ions and superconducting electrons in $\mathrm{Sm_{2-x}Ce_xCuO_{4-y}}$ may be large, with a value of approximately $\mathcal{J}\approx 60-110$ meV. The exchange interaction between conduction electron spins $\mathbf{S}$ and a rare-earth ion with total angular momentum $\mathbf{J}$ is given by[13]

$$\mathcal{H}=-2(g_J-1)\mathcal{J}(\mathbf{J}\cdot\mathbf{S})\ , \tag{1}$$

where g_J is the usual Landé g factor of the rare-earth ion. On general grounds, Abrikosov-Gor'kov pair-breaking theory[14] predicts that the magnetic pairbreaking resulting from such an interaction will scale with the exchange scattering rate, $1/\tau$, or, alternately, by the pair-breaking energy parameter,[15] $2\alpha=h/2\pi\tau$. The scattering rate is given by[13]

$$1/\tau=2\pi n h^{-1}N(\varepsilon_F)\mathcal{J}^2(g_J-1)^2J(J+1)\ , \tag{2}$$

where n is the concentration of paramagnetic rare-earth ions, h is Planck's constant, and $N(\varepsilon_F)$ is the density of electronic states at the Fermi energy ε_F. The degree of depression of the superconducting transition temperature T_c from its value in the absence of rare-earth magnetic ions, T_{c0}, is determined by the strength of α compared to its critical value, $\alpha_{\mathrm{cr}}=0.882k_BT_{c0}$, at which $T_c=0$. The full dependence is given by the digamma function, $\psi(z)=d[\ln\Gamma(z)]/dz$, where $\Gamma(z)$ is the usual gamma function. The form is[15]

$$\ln\left[\frac{T_c}{T_{c0}}\right]=\psi\left[\frac{1}{2}\right]-\psi\left[\frac{1}{2}+\frac{\alpha}{2\pi k_BT_c}\right]\ , \tag{3}$$

where k_B is Boltzmann's constant. As is generally observed, Eq. (3) predicts that T_c is a linearly decreasing function of α for small α, and decreases more rapidly as α_{cr} is approached. Note that α is also proportional to the de Gennes factor of the rare-earth ion in question, $(g_J-1)^2J(J+1)$. For small α, the expansion of the digamma function gives[15]

$$T_c=T_{c0}-(\pi\alpha/4k_B)\ . \tag{4}$$

For the electron-doped 2:1:4 materials, variations of the rare-earth hosts and/or dopant ions result in variations in superconducting properties. It has been pointed out[16] that such variations do *not* correlate with rare-earth magnetic properties. For example, in the lanthanide series $L_{2-x}\mathrm{Ce}_x\mathrm{CuO}_{4-y}$, note the monotonic trend: The $L=\mathrm{Gd}$ compound is nonsuperconducting, the lowest-T_c superconducting compound occurs for $L=\mathrm{Eu}$, with increasingly higher T_c's for L=Sm and Nd; the corresponding de Gennes factors are scattered: 15.75, 0, 4.46, and 1.84, respectively. Since magnetic properties apparently have at most a secondary effect on T_c, attempts have been made to correlate superconducting properties with intralayer and/or interlayer spacings.[16,17] For the purposes of this discussion, it is sufficient to note that the L=Sm system has one of the highest T_c's of the series, so that any magnetic pair-breaking effects cause at most a $\Delta T_c \leq 2$ K. For any reasonable estimate of the density of states $N(E_F)$, Eqs. (2) and (4) immediately imply

$$\mathcal{J} = \left[\frac{8k_B\,\Delta T_c}{\pi n N(\varepsilon_F)(g_J-1)^2 J(J+1)} \right]^{1/2} \leq 10 \text{ meV} , \tag{5}$$

where a conservative value of $N(\varepsilon_F)=1$ state eV^{-1} atom^{-1} has been used to obtain an upper bound on $\mathcal{J}$ [values of $N(\varepsilon_F)$ between 1 and 10 states eV^{-1} atom^{-1} are typically obtained for the various high-T_c copper oxides[18,19]]. Of course, if the small decrease in T_c is not largely attributable to magnetic effects, and/or a less conservative estimate is made, one would conclude an even smaller $\mathcal{J} \leq 1$ meV. Thus the value $\mathcal{J} \approx 60-110$ meV suggested by upper critical field measurements presents considerable difficulties for conventional pair-breaking theory. (Note also that since $\Delta T_c \propto \mathcal{J}^2$, such large $\mathcal{J}$ values would have a truly overwhelming effect on T_c.) We point out that in other magnetic superconductors, such anomalous behavior is not observed: For example, in $SmRh_4B_4$, upper critical field measurements[20] indicate that $\mathcal{J} \approx 23$ meV, and a corresponding, large, zero-field value of $\Delta T_c \approx 8$ K (compared to YRh_4B_4) is indeed observed. With these considerations in mind, it is apparent that further investigation is warranted.

Below, we attempt to estimate an upper limit on the rare-earth–conduction-electron exchange constant $\mathcal{J}$ by observing its effect on the net exchange coupling $\mathscr{J}$ between two rare-earth ions. This is done by comparative magnetic dilution; we simply use isovalent substitution to account for the changes due merely to dilution, and observe the concentration-dependent $\mathscr{J}$ that occurs with electron doping or hole doping. We are then particularly interested in any additional concentration dependence of $\mathscr{J}$ that accompanies the insulator-metal transition; such a contribution would be attributable to indirect exchange as described below; first, a brief preliminary discussion of magnetic dilution is in order.

Theories of magnetic dilution tend to differ for a number of specific predictions;[21] however, various available results, including those obtained by effective-Hamiltonian or effective-field,[22,23] cluster-expansion or cluster-variation,[24–26] and modern renormalization-group[27,28] techniques all give similar results for the case of interest here. The results are supported by Monte Carlo[29] and experimental[30–33] data. Many calculations are limited to the ferromagnetic case or to spin-$\frac{1}{2}$ systems with nearest-neighbor Heisenberg, XY, or Ising coupling. Real complications, such as extended interactions, spins other than $\frac{1}{2}$, anisotropy, multiple spin species, and complex lattice structures, have rarely received treatment. Fortunately, differences arising from such complications primarily affect parameters such as the critical concentration and critical exponents; the concentration dependence of the magnetic ordering temperature for mild dilution ($\leq 10\%$), of interest here, has been shown to be relatively insensitive to spin value and detailed lattice structure in numerous studies. We thus adopt a simple effective Hamiltonian approach,[22] with the intent of isolating steric and electronic effects from those of simple dilution.

The Sm^{3+} ions in Sm_2CuO_4 exhibit a mean-field-like transition[34] to an antiferromagnetically ordered state with a Néel temperature T_N of approximately 6 K. This is confirmed by specific-heat measurements,[35,36] which show a sharp anomaly at $T_N = 5.94$ K. Single-crystal susceptibility behavior[34] indicates that the easy axis of magnetization at low temperatures is parallel to the tetragonal c axis; thus an Ising model is appropriate. The detailed magnetic structure has not yet been determined by neutron diffraction.[37] We consider the result for a sublattice with z nearest neighbors on the second sublattice:[22]

$$T_N = \frac{|\mathscr{J}|}{k_B \ln \left[\dfrac{p'(z-1)+1}{p'(z-1)-1} \right]} , \tag{6}$$

where p' is the concentration of nonisolated magnetic ions, given by $p' = p[1-(1-p)^z]$, where p is the concentration of magnetic ions. For mild dilution, $p \approx p'$. Let $x = 1-p$ be the concentration of diluting ions. Then for small x expansion of Eq. (6) implies

$$T_N(x) \approx T_{N0}[1-(2(z-1)/\{z(z-2)\ln[z/(z-2)]\})x + O(x^2)] . \tag{7}$$

Thus, the normalized initial concentration dependence of the Néel temperature is linear with a slope that depends only, and weakly, on the number of nearest neighbors, with $-(1/T_{N0})dT_N/dx \approx 1.082$, 1.028, and 1.014 for z=4, 6, and 8, respectively. Such analysis assumes all other factors are equal; obviously, variations in the exchange coupling $\mathscr{J}$ between nearest neighbors due to steric or electronic effects will cause additional variations in T_N.

Finally, we consider the contribution $\mathscr{J}'$ to the net Sm-Sm exchange coupling $\mathscr{J}$ from Sm-ion–conduction-electron indirect exchange $\mathcal{J}$. This is the well-known RKKY interaction,[38–40], given in convenient form for a three-dimensional free electron gas by[41]

$$\mathscr{J}' = -\frac{\mathcal{J}^2}{\varepsilon_F} \frac{(k_F a_0)^6}{\pi^3} \left[\frac{\sin(2k_F R) - 2k_F R \cos(2k_F R)}{(2k_F R)^4} \right] , \tag{8}$$

where k_F is the Fermi wave vector, a_0^3 is the unit cell volume, and R is the magnetic ion separation. (An erroneous factor of 2^{-6} in Ref. 41 has been omitted.) Although a two-dimensional tight-binding expression might be more appropriate for the copper oxides, we know of no such calculation for the RKKY interaction. Instead, we note that for the crude estimates below, Eq. (8) contains the essential features of a second-order perturbation calculation of indirect exchange: that $\mathcal{J}' \approx \mathcal{j}^2/\varepsilon_F$ times a factor of order unity (or more accurately, $\sim 10^{-2}$) which includes a decaying oscillatory function. We point out that since the density of itinerant states in the copper oxides is relatively low (and thus k_F is relatively small), one might then expect that the first node in the RKKY oscillations is beyond the nearest neighbors, so that any appreciable $\mathcal{J}'$ probably contributes a ferromagnetic contribution[42] to the net antiferromagnetic nearest-neighbor $\mathcal{J}$.

IV. RESULTS AND DISCUSSION

In Fig. 1 are shown magnetic susceptibility data as a function of temperature at low temperatures for various $Sm_{2-x}Y_xCuO_4$ samples in the range $0 \le x \le 0.3$. Since the susceptibility cusps are somewhat rounded for these polycrystalline materials, we estimate the Néel temperatures from the intersection of the extrapolated susceptibility data below and above the cusp. For the $x=0$ specimen, we obtain $T_N = 6.01 \pm 0.05$ K, in fair agreement with the value $T_N = 5.94$ K obtained by specific-heat measurements.[35] Since Y^{3+} is isovalent with Sm^{3+}, it is not surprising that our resistivity data show that the entire series are, like the parent compound Sm_2CuO_4, semiconducting and, at low temperatures, insulating. Similar polycrystalline resistivity data have been reported previously and are not repeated here.[1–3,43] As has been previously noted,[36] the Néel temperatures in this rare-earth system are relatively large, indicative of strong exchange interactions. The effect of magnetic dilution is evident in Fig. 1; as expected, T_N decreases smoothly with increasing dilutant concentration. One can also observe that the peak value of the susceptibility increases and that the data above T_N shift upward, behavior due to both the lower Néel temperature and the correspondingly higher (less negative) Curie-Weiss temperature.

Similar magnetic susceptibility data as a function of temperature at low temperatures are shown in Fig. 2 for various $Sm_{2-x}Ce_xCuO_4$ samples in the range $0 \le x \le 0.2$. In this case, similar behavior is observed for the decrease in the Néel temperature, with quantitative differences discussed below. An additional feature is present for M=Ce: The monotonic upward shift in the susceptibility observed for M=Y again occurs for the separate ranges x=0–0.10 and 0.15–0.20, but a noticeable diamagnetic shift occurs over the x=0.10–0.15 range. This may be due to a subtle electronic or structural transition, or perhaps is attributable to a trace superconducting phase in these oxygen-annealed, otherwise-insulating samples. However, the latter explanation is not supported by low-field (H=10 Oe) magnetization data. Another explanation may involve a microscopic phase separation in the

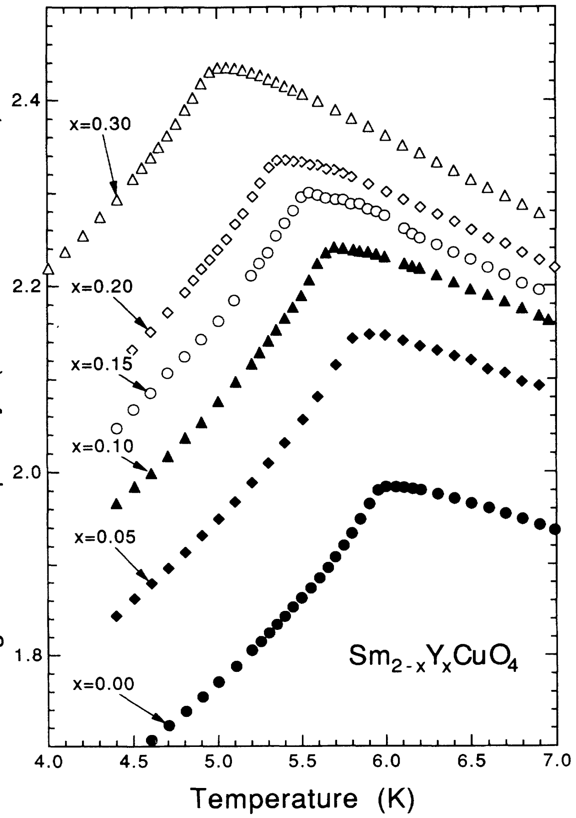

FIG. 1. Molar magnetic susceptibility χ_M data as a function of temperature T at low temperatures for $Sm_{2-x}Y_xCuO_4$ polycrystalline samples with various x in the range x=0–0.3.

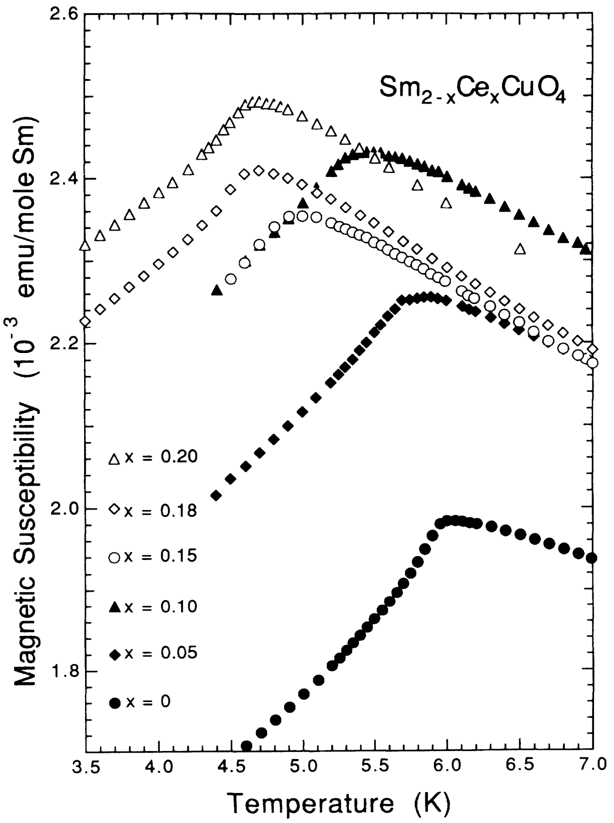

FIG. 2. Molar magnetic susceptibility χ_M data as a function of temperature T at low temperatures for $Sm_{2-x}Ce_xCuO_4$ polycrystalline samples with various x in the range x=0–0.2.

M=Ce system, as suggested by neutron diffraction[44] for the $\mathrm{Nd}_{2-x}\mathrm{Ce}_x\mathrm{CuO}_{4-y}$ system.

The high-temperature behavior of the magnetic susceptibility is not a strong function of concentration in $\mathrm{Sm}_{2-x}M_x\mathrm{CuO}_4$ for either M=Y or Ce. A representative set of data for $\mathrm{Sm}_{1.90}\mathrm{Y}_{0.10}\mathrm{CuO}_4$ is shown by the symbols in Fig. 3. Similar to previous analysis[45] for undoped $\mathrm{Sm}_2\mathrm{CuO}_4$, the magnetic susceptibility of the Sm^{3+} ions above T_N can be well described[46] by a Curie-Weiss contribution from the $J=\frac{5}{2}$ ground-state multiplet, plus a temperature-independent Van Vleck contribution from the admixture of the low-lying $J=\frac{7}{2}$ multiplet at an average energy $k_B\Delta E$ above the ground state:

$$\chi_M = N_A \left[\frac{\mu_{\mathrm{eff}}^2}{3k_B(T-\Theta)} + \frac{20\mu_B^2}{7k_B\Delta E} \right] , \tag{9}$$

where χ_M is the molar susceptibility, N_A is Avagodro's number, μ_{eff} is the effective moment per Sm ion, Θ is the Curie-Weiss temperature, and μ_B is the Bohr magneton. A fit to Eq. (9) is shown by the solid line in Fig. 3.

The extracted values of the splitting ΔE, the effective moment μ_{eff}, and the Curie-Weiss temperature Θ are shown in Figs. 4(a), 4(b), and 4(c), respectively. Data for $\mathrm{Sm}_{2-x}M_x\mathrm{CuO}_4$ with $x=0$–0.20 and both M=Y and Ce are shown. As might be expected for well-localized $4f$ moments, neither isovalent dilution nor dilution accompanied by electron doping has any appreciable effect on ΔE or μ_{eff}, which exhibit average values of 1060 K and $0.35\mu_B$, respectively, similar to the values $\Delta E=1150$ K and $\mu_{\mathrm{eff}}=0.33\mu_B$ reported previously[45] for $\mathrm{Sm}_2\mathrm{CuO}_4$. Some scatter in the values of the extracted parameters is apparent, possibly due to the difficulty of a three-parameter fit. The isovalent dilution only gradually affects the value of the Curie-Weiss temperature; the solid line in Fig. 4(c) for M=Y indicates a variation of $d\Theta/dx \approx 0.06$ K/at. %. For M=Ce, the increase is more dramatic, with $d\Theta/dx \approx 0.22$ K/at. %. These results will be discussed below, in light of the somewhat more accurately determined variations of T_N with concentration. It is noteworthy that the Curie-Weiss and Néel temperatures are nearly equal in magnitude, probably indicating that second-nearest-neighbor interactions are of little importance; a simple-mean-field model[47] would imply that second-nearest-neighbor (same-sublattice) interactions are down by a factor of $|(T_N+\Theta)/(T_N-\Theta)| \approx 0.05$ with respect to nearest-neighbor interactions.

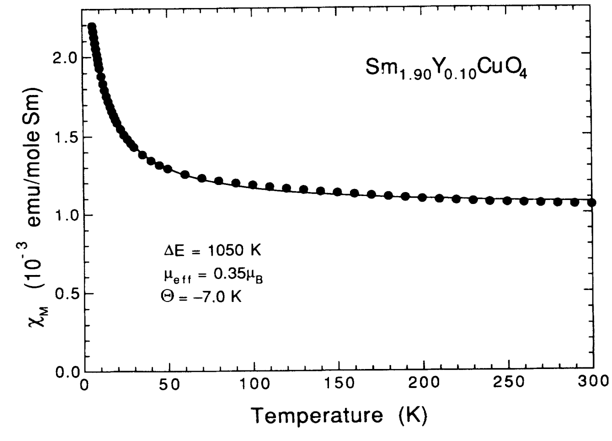

FIG. 3. Molar magnetic susceptibility χ_M as a function of temperature T over the temperature range 7–300 K for a typical sample, $\mathrm{Sm}_{1.90}\mathrm{Y}_{0.10}\mathrm{CuO}_4$. Symbols: experimental data; line: fit to the Curie-Weiss and Van Vleck contributions of Eq. (9).

Tetragonal unit cell parameters a and c are shown for $\mathrm{Sm}_{2-x}M_x\mathrm{CuO}_4$ in Figs. 5(a) and 5(b), respectively. Data for M=Ce, Y, and La are included. The relevant ionic radii[48] for isovalent La^{3+}, Sm^{3+}, and Y^{3+} are 1.160, 1.079, and 1.019 Å, respectively; thus, La and Y straddle Sm in size and provide an ideal range to determine steric effects. Such variation is evident in Fig. 5; both a and c increase (decrease) with La (Y) doping. For electron doping with the smaller Ce^{4+} (ionic radius 0.97 Å), a increases while c decreases, as has been previously reported and discussed[1,5,16,17] for $L_{2-x}M_x\mathrm{CuO}_4$ and $\mathrm{Sr}_{1-y}\mathrm{Nd}_y\mathrm{CuO}_2$. Two effects occur: Electron doping into the antibonding orbitals of the CuO_2 sheets stretches the Cu—O bond length and increases a, while substitution of the smaller Ce^{4+} for the larger Sm^{3+} decreases the spacing between the CuO_2 sheets, i.e., decreases c. Since changing a alters the Sm-Sm nearest-neighbor spacing, it

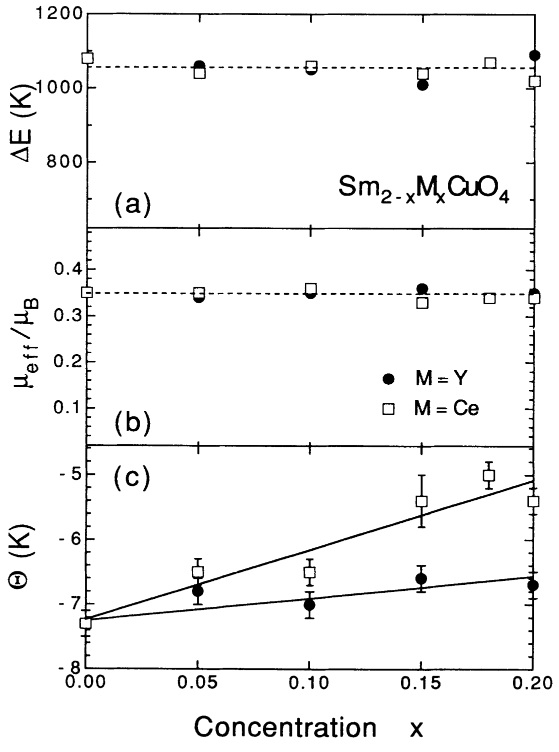

FIG. 4. (a) Extracted values of the energy splitting ΔE as a function of concentration x for both M=Ce (squares) and Y (circles) in $\mathrm{Sm}_{2-x}M_x\mathrm{CuO}_4$. The dashed line is the average value, $\Delta E=1060$ K. (b) Similarly, but for the extracted values of the effective moment, μ_{eff}; dashed line is the average value, $\mu_{\mathrm{eff}}=0.35\mu_B$. (c) Similarly, but for the extracted values of the Curie-Weiss temperature Θ. The solid lines are linear fits with slopes $d\Theta/dx=0.06$ K/at. % and 0.22 K/at. % for M=Y and Ce, respectively.

is important to note that isovalent La doping can produce as large a change in a as electron doping does; thus one can separate electronic and size effects.

The primary differences between isovalent dilution, steric effects, and electron doping are evident in Fig. 6, where the Sm^{3+} Néel temperature has been plotted as a function of concentration for various dopant ions M in $Sm_{2-x}M_xCuO_4$. For $M=Y$ and La (isovalent dilution), essentially linear decreases with concentration are observed; the solid line is a fit of the $M=Y$ data to the full form of Eq. (6) with $z=4$. (Although the precise magnetic structure has not been determined,[37] there are four nearest neighbors at a distance a from any given Sm ion; a simple linear least-squares fit to the data yields a normalized slope of $-(1/T_{N0})dT_N/dx=1.10$, further supporting [see the discussion following Eq. (7)] the supposition that $z=4$ is appropriate.) The full fit to Eq. (6) yields a Sm-Sm exchange constant $\mathcal{J}=-0.36$ eV. As mentioned above, this value is in theory determined completely by the initial Néel temperature; the variation with concentration follows the universal form of Eq. (6), without adjustable parameters. Thus an important observation is that for $M=Y$ there is no measurable steric effect; it is closest to Sm in size, and essentially behaves as a simple, ideal magnetic dilutant. If any steric effect for the smaller $M=Y$ exists, the slight lattice contraction presumably results in a small increase in $|\mathcal{J}|$ (and thus in T_N). For $M=La$, only a small effect is evident; the larger La ions apparently cause a minor additional decrease in the Néel temperature and thus are indicative of an exchange coupling decreasing slightly with concentration as the lattice expands. The dashed line in Fig. 6 is a linear fit with slope $-(1/T_{N0})dT_N/dx=1.26$, a somewhat larger slope than expected for mere dilution. Note from the values of the lattice constant a in Fig. 5 that if the coupling in the direction of the tetragonal basal plane is dominant (i.e., in the direction of Sm nearest neighbors), the steric effect of La substitution should exceed that of Ce.

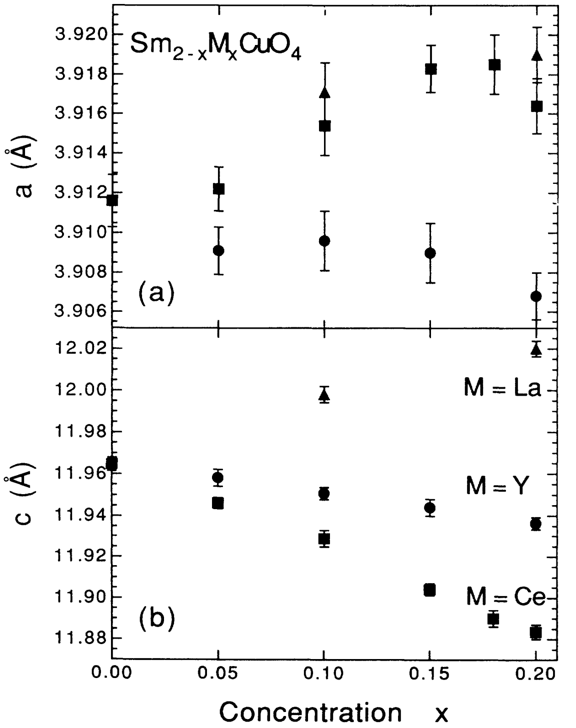

FIG. 5. (a) Tetragonal lattice constant a as a function of concentration x in $Sm_{2-x}M_xCuO_4$ for $M=La$ (triangles), Ce (squares), and Y (circles). (b) Similarly, but for tetragonal lattice constant c.

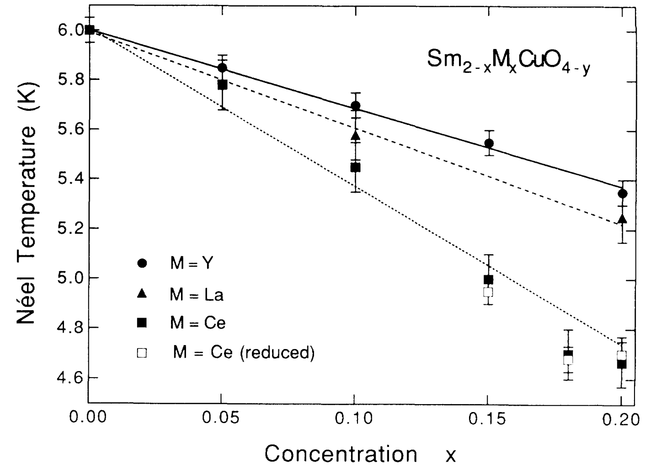

FIG. 6. Néel temperature T_N as a function of concentration x for $Sm_{2-x}M_xCuO_4$ for $M=Y$ (circles), La (triangles), and Ce for both oxygenated (solid squares) and reduced (open squares) samples. The solid curve is a fit to Eq. (6), yielding $|\mathcal{J}|=0.36$ meV. The dashed and dotted lines are linear fits with slopes given by $-(1/T_{N0})dT_N/dx=1.26$ and 2.21 for $M=La$ and Ce, respectively, with $T_{N0}=6.01$ K.

For electron doping, the data of Fig. 6 indicate that a much more rapid depression of the Néel temperature occurs than in either case of mere dilution. Data for $M=Ce$ are shown for both oxygen-annealed (insulating, solid symbols) and helium-reduced (metallic, open symbols) specimens; the reduced $x=0.15$ and $x=0.18$ samples are metallic and superconducting, while the reduced $x=0.20$ sample is metallic. The dotted line in Fig. 6 is a linear fit to all of the $M=Ce$ data and has slope $-(1/T_{N0})dT_N/dx=2.21$. As is evident, no appreciable change occurs upon helium reduction. Thus the manner in which electron doping affects Sm-Sm coupling apparently does not depend on whether or not the electrons are delocalized, although the same electrons may be responsible in both cases. We note, however, that there appears to be a shift in the concentration dependence, with the data in the $x=0$–0.10 range above the linear fit and those in the $x=0.15$–0.20 range below the fit. Thus one may again speculate (see the discussion of Fig. 2, above) that a concentration-dependent electronic or structural transition occurs in the $x=0.10$–0.15 range of even the insulating series.

With the analytic form of Eq. (6), it is a simple matter to reexpress data of Fig. 6 in terms of concentration-dependent exchange constants; this has been done in Fig. 7, where the magnitude of $\mathcal{J}$ is plotted as a function of concentration for $M=Sr$, Y, La, and Ce. One can see im-

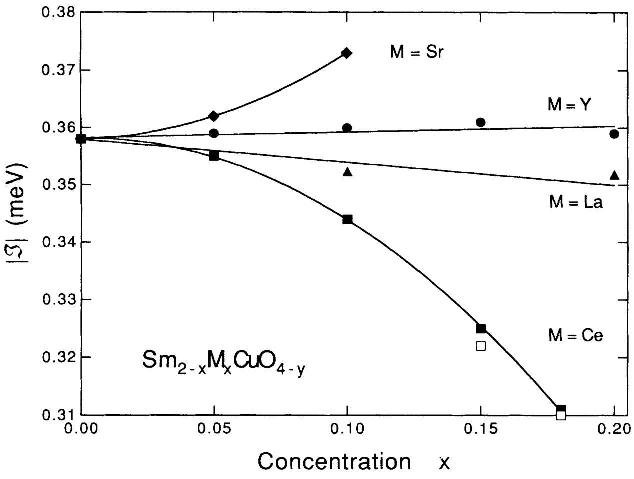

FIG. 7. Magnitude of the extracted values of the Sm-Sm exchange coupling $|\mathcal{J}|$ as a function of concentration x in $Sm_{2-x}M_xCuO_{4-y}$ for M=Sr (diamonds), Y (circles), La (triangles), and Ce for both oxygenated (solid squares) and reduced (open squares) samples. Solid lines are guides to the eye. Values of $|\mathcal{J}|$ were obtained from experimental Néel temperatures using the dilution theory of Eq. (6).

mediately that electron doping (M=Ce) decreases $|\mathcal{J}|$, while hole doping (M=Sr) enhances it. More importantly, the figure reiterates a main result from the M=Ce data: No appreciable change in the exchange constant $\mathcal{J}$ occurs as the insulator-metal transition is crossed, and none occurs as metallic behavior improves (various transport measurements[1,49,50] indicate that the reduced materials become increasingly more metallic at high concentrations). From the data of Fig. 7, we estimate an upper bound for an excess conduction-electron contribution $\mathcal{J}'$ to the total $\mathcal{J}$ to be $\mathcal{J}' \leq 0.005$ meV. If one instead adopts a more restrictive picture that, in some manner, all of the electron-doping effect on Sm-Sm coupling is suddenly transferred to the conduction electrons upon delocalization, a larger contribution $\mathcal{J}' \approx 0.03$ eV at $x=0.15$ would be estimated from Fig. 7.

It is a somewhat difficult matter to translate such a $\mathcal{J}'$ into an accurate bound on the exchange coupling $\mathscr{J}$ between the rare-earth ions and the conduction electrons; this is of interest, since, as discussed above, an anomalously large value of $\mathscr{J}$ in the copper oxides presents difficulties for pair-breaking theory. We first make a crude estimate for a three-dimensional free electron system: For electron doping with 0.15 electron per Cu atom, $k_F=[3\pi^2(2\times0.15)/a^2c]^{1/3}\approx 1.44/a$. Using the limit $\mathcal{J}' \leq 0.005$ meV obtained above, one can then estimate from Eq. (9) that $\mathscr{J} \leq 3$ meV. An improvement might be obtained by using the two-dimensional value, $k_F=[2\pi\times0.15/a^2]^{1/2}\approx 0.97/a$, and by incorporating the fact that this is presumably a narrow-band material, e.g., using an effective mass $m^* \approx 10m$. One then obtains $\mathscr{J} \leq 6$ meV. If we relax the estimate $\mathcal{J}' \leq 0.005$ meV and instead assume $\mathcal{J}' \approx 0.03$ meV as discussed in the last paragraph, an increase of only a factor of $6^{1/2}$ is obtained, i.e., the same calculations give $\mathscr{J}=7-15$ meV. In any case, we are led to the conclusion that our estimate of the coupling is small, perhaps very small. From these results, we conclude that the requirement of pair-breaking theory determined above ($\mathscr{J} \leq 10$ meV) is not violated here, and that previous values ($\mathscr{J} \approx 60-100$ meV) were overestimated.

V. SUMMARY

We have presented primarily magnetic data which attempt to isolate and quantify the various effects of size, dilution, and electron and hole doping on rare-earth magnetism in $Sm_{2-x}M_xCuO_4$ for various nonmagnetic substituents ($M=Ce^{4+}$, Y^{3+}, La^{3+}, and Sr^{2+}). We report good agreement with a simple theory of magnetic dilution for the M=Y case, and note a small effect associated with size for the larger M=La substitution. For M=Ce, we observe some behavior suggestive of a subtle electronic or structural transition in the range $x=0.10-0.15$, even for the insulating series. For the reduced, metallic series, we see no evidence of additional Sm-Sm coupling accompanying the insulator-metal transition. However, an appreciable depression (enhancement) of the Sm-Sm coupling is observed for electron (hole) doping, whether or not the charges are delocalized. Difficulties suggested by previous data concerning the applicability of pair-breaking theory in these materials are apparently not substantiated; our best estimates of rare-earth–conduction-electron exchange couplings are relatively low, $\mathscr{J} \lesssim 6$ meV. Future work on single crystals is recommended to further investigate the detailed concentration dependence and anisotropy of these materials.

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