Antiferromagnetic ordering in superconducting and oxygen-deficient nonsuperconducting RBa$_2$Cu$_3$O$_{7-\delta}$ compounds (R = Nd and Sm)

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Low-temperature (0.5–4 K) specific-heat measurements have been made on oxygen-deficient ($\delta \approx 0.5$) nonsuperconducting RBa$_2$Cu$_3$O$_{7-\delta}$ (R = Nd and Sm) compounds and compared to measurements previously performed on their high-critical-temperature $T_c \approx 92$ K superconducting counterparts ($\delta \approx 0.1$). We show that the specific-heat anomaly due to magnetic ordering of the Nd^{3+} and Sm^{3+} ions in the $T_c \approx 92$ K superconducting RBa$_2$Cu$_3$O$_{7-\delta}$ (R = Nd and Sm) compounds can be well described by a two-dimensional anisotropic antiferromagnetic Ising model with exchange-interaction parameters E_1 and E_2 in the a-b plane; the respective values of the Néel temperature T_N and the ratio E_1/E_2 are 0.5 K and 50 for Nd and 0.61 K and 11 for Sm. The specific-heat anomaly of the oxygen-deficient nonsuperconducting NdBa$_2$Cu$_3$O$_{7-\delta}$ compound is also associated with an antiferromagnetic transition according to low-temperature magnetization measurements, although the temperature dependence of the anomaly and the value of T_N (~ 1.7 K) are quite different from those in the superconducting state. Neutron-diffraction measurements on the $T_c \approx 92$ K superconducting phase of NdBa$_2$Cu$_3$O$_{7-\delta}$ reveal that the Nd^{3+} magnetic moments form a simple antiferromagnetic structure in which the nearest-neighbor moments in all three dimensions are aligned antiparallel to one another along the c axis. In the $T_c \approx 92$ K superconducting phase, the ordered moment of the Nd^{3+} ions obtained from the neutron scattering data is $\langle \mu_z \rangle = (1.07 \pm 0.07)\mu_B$. The low-temperature specific-heat anomaly of the oxygen-deficient nonsuperconducting SmBa$_2$Cu$_3$O$_{7-\delta}$ compound can be formally described by a Schottky anomaly for two doublets split by the crystalline electric field or a one-dimensional Ising model.

I. INTRODUCTION

The discovery of the series of RBa$_2$Cu$_3$O$_{7-\delta}$ (R is a rare-earth element, except for Ce, Pr, Pm, and Tb) magnetic superconductors with high superconducting critical temperatures (T_c) near 90 K has raised many interesting questions concerning the interaction between the R^{3+} magnetic moments and the superconducting electrons in these materials.[1,2] Whereas there is, as yet, no definitive evidence that superconducting properties such as T_c (Ref. 2) and the initial slope of the upper-critical-field H_{c2} curve $(-dH_{c2}/dT)_{T_c}$,[3,4] depend significantly on the R^{3+} ions in the series of RBa$_2$Cu$_3$O$_{7-\delta}$ compounds, other physical properties, particularly those of magnetic character, exhibit substantial variations with the R^{3+} ions.[5]

The negligible effect of the R^{3+} ions on T_c indicates that the exchange interaction between the spin **s** of the superconducting electrons and the angular momentum **J** of the R^{3+} ions is small, since R^{3+} ions with partially filled $4f$ electron shells ordinarily depress T_c through pair-breaking effects at a rate that scales with the pair-breaking parameter

$$\alpha \equiv n\hbar^{-1}N(E_F)\mathcal{J}^2(g_J-1)^2J(J+1)\ , \tag{1}$$

where n is the concentration of paramagnetic R^{3+} ions, $N(E_F)$ is the density of conduction electron states at the Fermi level, $\mathcal{J}$ is the exchange interaction parameter, and g_J and J are, respectively, the Landé g factor and total angular momentum of the R^{3+} ions.[6] A small value of $\mathcal{J}$ indicates minimal overlap between the R^{3+} $4f$ orbital wave functions and the wave functions of the neighboring copper and oxygen atoms. The RBa$_2$Cu$_3$O$_{7-\delta}$ compounds have layered orthorhombic perovskitelike crystal structures containing CuO_2 planes and CuO chains;[7] the charge carriers involved in the superconductivity are generally believed to be holes in the CuO_2 planes,[8] whose concentration is governed by the concentration of oxygen vacancies in the CuO chains.[9,10]

The marked variation with the R^{3+} ions of a number

of physical properties of the RBa$_2$Cu$_3$O$_{7-\delta}$ compounds can be traced to both intraionic and interionic effects. The R^{3+} intraionic effects, which are associated with the internal electronic structure of the $4f$ shell modified by the crystalline electric field (CEF) are manifested in the anisotropy of the paramagnetic susceptibility due to the R^{3+} ions[11] and Schottky anomalies in the low-temperature specific heat, which are particularly prominent for the RBa$_2$Cu$_3$O$_{7-\delta}$ compounds with R=Ho, Tm, and Yb.[12,13] The R^{3+} interionic effects appear to be due to dipolar, superexchange, and Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions between the R^{3+} magnetic moments, which lead to long-range antiferromagnetic ordering of the R^{3+} ions at temperatures in the vicinity of $\sim$1 K which coexists with the superconductivity. Evidence of magnetic ordering of the R^{3+} ions in the RBa$_2$Cu$_3$O$_{7-\delta}$ compounds has emerged from specific-heat measurements on the compounds with R=Nd,[2,14] Sm,[2,14,15] Gd,[2,14-21] Dy,[2,14-16,20] Ho,[22] and Er,[2,14,16,20,22] and Mössbauer effect measurements on the compound with R=Yb.[23] The magnetic ordering temperatures inferred from the sharp peaks in the $C(T)$ contributions associated with magnetic order[2,14,22] range from 0.17 K for R=Ho to 2.25 K for R=Gd. The onset of the hyperfine splitting for the Yb compound yields a magnetic ordering temperature of $\sim$0.35 K.[23] The shapes of the $C(T)$ anomalies due to magnetic ordering for the RBa$_2$Cu$_3$O$_{7-\delta}$ compounds with R=Sm, Gd, and Er have been analyzed in terms of antiferromagnetic two-dimensional (2D) and three-dimensional (3D) Ising models with isotropic exchange interactions and are found to be best described by the 2D Ising model.[24-27] The occurrence of antiferromagnetic order has been directly verified for the Gd, Dy, and Er compounds by means of neutron scattering experiments. In the cases of Gd (Ref. 28) and Dy,[29,30] the ordered R^{3+} magnetic moments are parallel to the c axis, whereas in the case of Er,[31,32] they lie in the a-b plane and are parallel to the b axis.

One way of exploring the interaction between the localized magnetic moments and the superconducting electrons would be to investigate the magnetic properties of the nonsuperconducting counterparts of the $T_c \approx 92$ K superconducting ($\delta \approx 0.1$) RBa$_2$Cu$_3$O$_{7-\delta}$ compounds. Nonsuperconducting RBa$_2$Cu$_3$O$_{7-\delta}$ compounds can be obtained by partially removing the oxygen until the oxygen-vacancy concentration δ increases from $\sim$0.1 to $\sim$0.5, at which point T_c vanishes and the crystal symmetry changes from orthorhombic to tetragonal.[9] It has been found that T_N and the shape of the specific-heat anomaly associated with the antiferromagnetic (AF) ordering of Gd ions is the same for both superconducting ($\delta \approx 0.1$) and oxygen-deficient nonsuperconducting ($\delta \approx 0.85$) GdBa$_2$Cu$_3$O$_{7-\delta}$.[18] As discussed below, there is some controversy[28,33,34] about whether or not the AF structure of GdBa$_2$Cu$_3$O$_{7-\delta}$ undergoes a subtle, but distinct, change between $\delta \approx 0.1$ and 0.5, based on neutron scattering experiments. However, the magnetic ordering inferred from low-temperature specific-heat measurements on the compounds with R=Er and Dy has been reported to change from 2D Ising to XY model behavior as the oxygen-vacancy concentration is increased and the superconductivity is reduced.[20] These results indicate that RKKY and superexchange interactions, as well as dipolar interactions, are responsible for the magnetic coupling in these compounds.

In this paper, we report the measurements of the specific-heat anomaly associated with the magnetic ordering of the R^{3+} ions in both $T_c \approx 92$ K superconducting ($\delta \approx 0.1$) and oxygen-deficient nonsuperconducting ($\delta \approx 0.5$) RBa$_2$Cu$_3$O$_{7-\delta}$ compounds (R=Nd and Sm) which reveal marked changes in the shape of the specific-heat anomaly and the Néel temperature when oxygen is removed. For fully oxygenated superconducting RBa$_2$Cu$_3$O$_{7-\delta}$ compounds with R=Nd and Sm, the specific-heat anomalies can be described by the two-dimensional antiferromagnetic Ising model with anisotropic exchange interactions in the a-b plane. The antiferromagnetic structure of the Nd^{3+} magnetic moments in the NaBa$_2$Cu$_3$O$_{7-\delta}$ compound with δ=0.1 has been determined from neutron scattering experiments. While the investigation of the magnetic ordering of the R^{3+} ions in the RBa$_2$Cu$_3$O$_{7-\delta}$ compounds is of interest in its own right, it may also yield information about the electronic structure of these materials which will eventually be able to account for their extraordinarily high T_c's and other remarkable superconducting properties. A preliminary account of the specific-heat experiments presented herein has been given in Ref. 5.

II. EXPERIMENTAL DETAILS

The superconducting RBa$_2$Cu$_3$O$_{7-\delta}$ samples for specific-heat measurements were prepared by a solid-state reaction of rare earth and copper oxides and barium carbonate as described in a previous report.[35] Neutron powder profile refinement measurements carried out on another superconducting NdBa$_2$Cu$_3$O$_{7-\delta}$ sample, prepared using the same solid-state reaction method, revealed a single-phase sample with an oxygen-vacancy concentration $\delta = 0.10 \pm 0.01$. The nonsuperconducting oxygen-deficient RBa$_2$Cu$_3$O$_{7-\delta}$ samples were obtained by heat treating the $T_c \approx 92$ K superconducting samples at $T_c \approx \sim$820–850 °C in air for 24 h, after which they were removed from the oven and allowed to cool quickly to room temperature. This procedure is very similar to that used to systematically reduce the T_c of YBa$_2$Cu$_3$O$_{7-\delta}$ by many other research groups.[9] The oxygen-vacancy concentration δ was estimated by measuring the sample weight loss after heat treating in air, assuming that $\delta \approx 0.1$ for the 92 K superconducting RBa$_2$Cu$_3$O$_{7-\delta}$ (R=Nd and Sm) starting materials. From the oxygen reductions of 0.38 for the Nd compound and 0.43 for the Sm compound, the nonsuperconducting compounds had the approximate composition RBa$_2$Cu$_3$O$_{6.5}$ (R=Nd and Sm).

Each of the RBa$_2$Cu$_3$O$_{7-\delta}$ compounds, before and after oxygen reduction, was characterized by means of powder x-ray diffraction and electrical resistivity measurements. The x-ray diffraction measurements revealed the expected layered orthorhombic perovskitelike structure for the superconducting samples and the related

tetragonal structure for the nonsuperconducting samples. The electrical resistivity of the R =Nd and Sm superconducting $RBa_2Cu_3O_{7-\delta}$ compounds exhibited metallic behavior in the normal state above T_c, and had the following values of T_c and transition width ΔT_c: R =Nd $-T_c$ =92 K and ΔT_c =4 K (specific-heat sample), and T_c =92 K and ΔT_c =3 K (neutron scattering sample); R =Sm $-T_c$ =91 K and ΔT_c =3 K. Here, T_c was defined as the temperature at which the electrical resistivity ρ dropped to 50% of its extrapolated normal-state value, while ΔT_c was defined as the difference between the temperatures at which ρ dropped to 90% and 10% of its extrapolated normal-state value. The electrical resistivity of the nonsuperconducting phases of the Nd and Sm compounds displayed semiconducting behavior with no sign of a superconducting transition down to ~4 K, a result that is consistent with the tetragonal structure of these oxygen-deficient compounds. The magnetization measurements were performed with SQUID and Faraday magnetometers, and the heat-capacity measurements were carried out in a semiadiabatic calorimeter using the heat-pulse technique in applied magnetic fields up to 5 kOe.

To determine the magnetic structure of the $NdBa_2Cu_3O_{7-\delta}$ compound, neutron-diffraction measurements were taken on a standard triple-axis spectrometer at the National Institute of Standards and Technology (formerly National Bureau of Standards) Research Reactor. A pyrolytic graphite PG(002) monochromater was employed, with a PG filter to suppress higher-order wavelength contaminations. The wavelength was 2.355 Å, and the angular collimations before and after the monochromator and after the sample were 60'-20'-20' (full width at half maximum), respectively. No analyzer crystal was used in these measurements. The sample was mounted in a top-loading ^{3}He-^{4}He dilution refrigerator with a low-temperature capability of ~25 mK.

III. RESULTS

A. Magnetic susceptibility

Shown in Fig. 1 are inverse magnetic susceptibility χ^{-1} versus temperature T data for both nonsuperconducting $RBa_2Cu_3O_{7-\delta}$ (R =Nd and Sm) compounds measured with a SQUID magnetometer in a field of 1 kOe for R =Nd and 10 kOe for R =Sm. Both sets of data can be described by the sum of a temperature-independent term χ_0 and a Curie-Weiss contribution, i.e.,

$$\chi(T)=\chi_0+N\mu_{\rm eff}^2/3k_B(T-\Theta)\ , \qquad (2)$$

TABLE I. Values of the effective moment $\mu_{\rm eff}$, Curie-Weiss temperature Θ, and the temperature-independent constant χ_0, for nonsuperconducting $RBa_2Cu_3O_{7-\delta}$ obtained from the fit of Eq. (2) to the data in Fig. 1.

	$\mu_{\rm eff}$ (μ_B)	Θ (K)	χ_0 (cm^3/mole)
Nd	2.50	−0.92	2.98×10^{-3}
Sm	0.86	0.13	9.21×10^{-4}

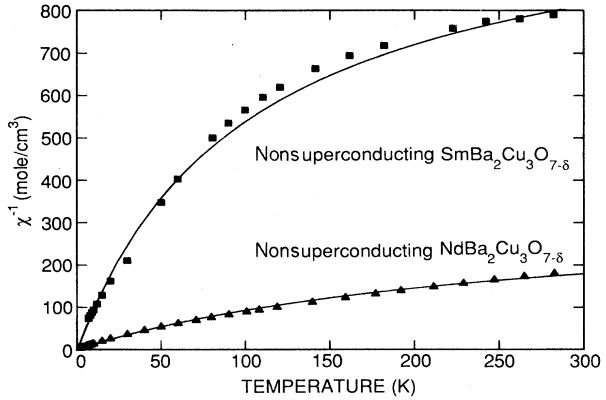

FIG. 1. Inverse magnetic susceptibility χ^{-1} vs temperature between 2 and 300 K for oxygen-deficient nonsuperconducting ($\delta\approx0.5$) $NdBa_2Cu_3O_{7-\delta}$ and ($\delta\approx0.5$) $SmBa_2Cu_3O_{7-\delta}$ compounds.

where N is Avogadro's number, k_B is Boltzmann's constant, $\mu_{\rm eff}$ is the effective magnetic moment of the R^{3+} ions, and Θ is the Curie-Weiss temperature. The values of these parameters, obtained from fits of Eq. (2) to the data (solid lines in Fig. 1), are listed in Table I. The values of $\mu_{\rm eff}$ for the nonsuperconducting compounds, $2.50\mu_B/Nd^{3+}$ and $0.86\mu_B/Sm^{3+}$, can be compared to the values of $\mu_{\rm eff}$ for the R^{3+} free ions, $3.62\mu_B/Nd^{3+}$ and $0.84\mu_B/Sm^{3+}$, and the superconducting compounds, $3.10\mu_B/Nd^{3+}$ and $1.32\mu_B/Sm^{3+}$.[36]

B. Low-temperature specific heat

The low-temperature specific heat of the superconducting $RBa_2Cu_3O_{7-\delta}$ compounds has been reported previously.[2,13,14] Shown in Fig. 2 are excess specific heat ΔC

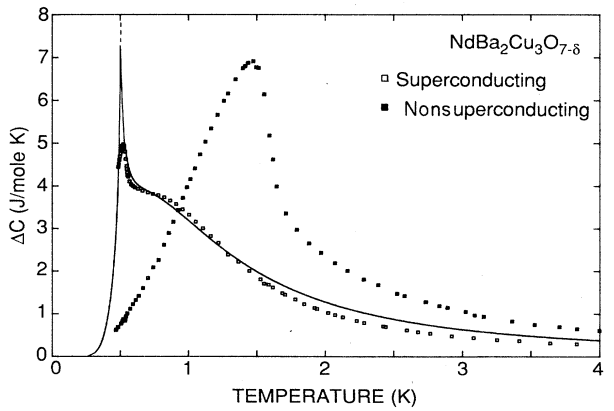

FIG. 2. Magnetic specific heat ΔC vs temperature for (a) $T_c\approx92$ K superconducting ($\delta\approx0.1$; open squares) and (b) oxygen-deficient nonsuperconducting ($\delta\approx0.5$; solid squares) $NdBa_2Cu_3O_{7-\delta}$. The solid line that has been fitted to the $\Delta C(T)$ data for $\delta\approx0.1$ represents the solution of the two-dimensional antiferromagnetic Ising model with a Néel temperature T_N=0.50 K and exchange-interaction parameters E_1=0.85 K and E_2=0.017 K.

(total specific heat minus the electron and lattice contributions estimated from the specific heat of the nonmagnetic $YBa_2Cu_3O_{7-\delta}$ compound) versus temperature T data in the range $0.5 \leq T \leq 4$ K for both superconducting and nonsuperconducting phases of $NdBa_2Cu_3O_{7-\delta}$. The electronic Schottky anomaly due to the splitting of the Hund's rules ground-state multiplet of the Nd^{3+} ions by the CEF, occurs at appreciably higher temperatures than the anomaly due to magnetic ordering of the R^{3+} ions, and can be neglected in this temperature range. For the superconducting $NdBa_2Cu_3O_{7-\delta}$ compound, the spike-shaped feature superimposed on a rounded peak in the specific heat is reminiscent of the calculated $C(T)$ curves for an anisotropic 2D antiferromagnetic Ising model with different exchange interactions along the two relevant directions in the lattice. The 2D character is presumably associated with predominantly nearest-neighbor interactions between Nd^{3+} ions along the a and b axes of the basal plane. We have used the Onsager solution to describe the specific heat of the Ising lattice which is given by the following expression:[37]

$$C(T)=k_B\frac{4\beta^2}{\pi}\left[\left[\frac{E_1}{\sinh(2\beta E_1)}\right]^2\coth(2\beta E_1)\coth(2\beta E_2)\times[\mathbf{K}(k_<)-\Pi_1(\operatorname{csch}^2(2\beta E_2),k_<)]\right.$$
$$+\left[\frac{E_2}{\sinh(2\beta E_2)}\right]^2\coth(2\beta E_1)\coth(2\beta E_2)\times[\mathbf{K}(k_<)-\Pi_1(\operatorname{csch}^2(2\beta E_1),k_<)]$$
$$\left.+2E_1E_2[\mathbf{K}(k_<)-\mathbf{E}(k_<)]\right] \tag{3}$$

for $T<T_N$, and

$$C(T)=k_B\frac{4\beta^2}{\pi}\left[\left[\frac{E_1}{\sinh(2\beta E_1)}\right]^2\cosh(2\beta E_1)\cosh(2\beta E_2)\times[\mathbf{K}(k_>)-\Pi_1(\sinh^2(2\beta E_1),k_>)]\right.$$
$$+\left[\frac{E_2}{\sinh(2\beta E_2)}\right]^2\cosh(2\beta E_1)\cosh(2\beta E_2)\times[\mathbf{K}(k_>)-\Pi_1(\sinh^2(2\beta E_2),k_>)]$$
$$\left.+2\frac{E_1E_2}{\sinh(2\beta E_1)\sinh(2\beta E_2)}[\mathbf{K}(k_>)-\mathbf{E}(k_>)]\right] \tag{4}$$

for $T>T_N$, where E_1 and E_2 are the interaction strengths along the two directions in a-b basal plane, $\beta=1/k_BT$,

$$k_>=\sinh(2\beta E_1)\sinh(2\beta E_2)\ ,$$
$$k_<=[\sinh(2\beta E_1)\sinh(2\beta E_2)]^{-1}\ ,$$

and the integrals

$$\mathbf{K}(k)=\int_0^{\pi/2}(1-k^2\sin^2\phi)^{-1/2}d\phi\ ,$$
$$\mathbf{E}(k)=\int_0^{\pi/2}(1-k^2\sin^2\phi)^{1/2}d\phi\ , \tag{5}$$

and

$$\Pi_1(\nu,k)=\int_0^{\pi/2}(1+\nu\sin^2\phi)^{-1}(1-k^2\sin^2\phi)^{-1/2}d\phi\ ,$$

are the complete elliptic integrals of the first, second, and third kinds, respectively. When performing the data analysis, the numerical values of the integrals $\mathbf{K}(k)$, $\mathbf{E}(k)$, and $\Pi_1(\nu,k)$ were calculated with the numerical algorithms reported in Refs. 38 and 39.

According to the Onsager solution, the Néel temperature T_N is determined from the interaction parameters E_1 and E_2 by means of the following relation:

$$1=\sinh(2\beta E_1)\sinh(2\beta E_2),\quad \beta=1/k_BT_N\ . \tag{6}$$

The value $T_N=0.52$ K for $NdBa_2Cu_3O_{7-\delta}$ is readily determined as the temperature of the divergence of the specific-heat data in Fig. 2. Therefore, the values of E_1 and E_2 must be chosen so that the calculated value of $T_N(E_1,E_2)$ agrees with the measured value of T_N. We have used the method of least squares to fit the data for $0.55 \leq T \leq 4$ K, yielding $E_1=0.85$ K and $E_2=0.017$ K for the exchange-interaction parameters and $T_N=0.50$ K for the corresponding Néel temperature, in good agreement with the experimental value. The fitted curve, represented by the solid line in Fig. 2, reflects the features in the $C(T)$ data including the sharp peak at T_N and the shoulder right above T_N. In this fit, the value of E_1 is approximately 50 times larger than that of E_2, which implies that the exchange interaction in the a-b plane is extremely anisotropic. It is not possible to account for such strong anisotropy of the exchange interaction in terms of the dipolar interaction, which was suggested to be the dominant interaction between the R^{3+} ions in the $RBa_2Cu_3O_{7-\delta}$ compounds on the basis of specific-heat measurements on superconducting and nonsuperconducting oxygen-deficient $GdBa_2Cu_3O_{7-\delta}$ compounds by Dunlap *et al.*[18] We have been studying the specific-heat anomaly due to magnetic ordering in $NdBa_2Cu_3O_{7-\delta}$ in applied magnetic fields, and have observed no significant

changes in either amplitude or shape of the anomaly for fields up to 5 kOe.

The low-temperature specific-heat anomaly, due to magnetic ordering for the nonsuperconducting $NdBa_2Cu_3O_{6.5}$ compound, is distinctly different from that of the superconducting samples, in both shape and temperature (1.47 K) of the peak. We have not yet been able to describe the specific-heat anomaly due to this magnetic transition, although the change of the entropy associated with it is $1.05R$ ln2 for $T \leq 4$ K, indicating that magnetic ordering arises out of a doublet ground state. This suggests that the configuration of the CEF ground state and the low-lying excited states of the Nd^{3+} ions are not appreciably changed in the oxygen-deficient nonsuperconducting material. Shown in Fig. 3 are the low-temperature magnetic susceptibility ($\equiv$magnetization applied magnetic field) data for this sample, measured with a Faraday magnetometer in fields of 1 and 10 kOe, which exhibit a break in slope indicative of antiferromagnetic order at ~ 1.7 K, consistent with the specific-heat measurements as well as the neutron scattering experiments described in Sec. III C.

Shown in Fig. 4 are excess specific-heat ΔC versus T data for $0.5 \leq T \leq 3$ K for both superconducting ($\delta \approx 0.1$) and nonsuperconducting oxygen-deficient ($\delta \approx 0.5$) $SmBa_2Cu_3O_{7-\delta}$ compounds. The specific heat of the superconducting samples can also be described by the Onsager solution for an anisotropic 2D Ising lattice. The least-squares fit of Eqs. (3) and (4) to the data for $0.5 \leq T \leq 3.0$ K yielded the values $E_1 = 0.70$ K and $E_2 = 0.063$ K for the exchange-interaction parameters, and, from Eq. (6), the value $T_N = 0.61$ K for the Néel temperature, which agrees very well with the measured value. For comparison, the specific heat calculated according to the Onsager solution for an isotropic 2D Ising lattice is indicated by the dashed curve in Fig. 4. The isotropic 2D solution clearly fails to describe the specific-heat data and the discrepancy far exceeds any errors associated with conduction electron, phonon, and electronic Schottky anomaly corrections. The ratio of the exchange-interaction parameter anisotropy, $E_1/E_2 \approx 11$, is sizable but smaller than that for the compound with $R = Nd^{3+}$.

The specific-heat anomaly of the nonsuperconducting oxygen-deficient $SmBa_2Cu_3O_{7-\delta}$ sample is also different from that of the superconducting sample. The excess specific heat ΔC versus temperature curve is "bell shaped" with a maximum ΔC_{max} at ~ 1.07 K, and is reminiscent of a Schottky-type anomaly rather than a transition to a long-range magnetically ordered state. Since Sm^{3+} is a Kramers ion, the $J = \frac{5}{2}$ Hund's rule ground state will presumably be split into three doublets by the CEF. The values of $\Delta C_{max} \approx 0.441R$ around 1 K and $S(5\text{ K}) = 1.02R$ ln2 suggest a two-level system for the Sm^{3+} ion in this temperature range, for which the specific heat has the following form:

$$C(T) = Nk_B(\beta E)^2 \frac{\exp(\beta E)}{[1+\exp(\beta E)]^2}, \tag{7}$$

where E is the energy difference between the two levels.

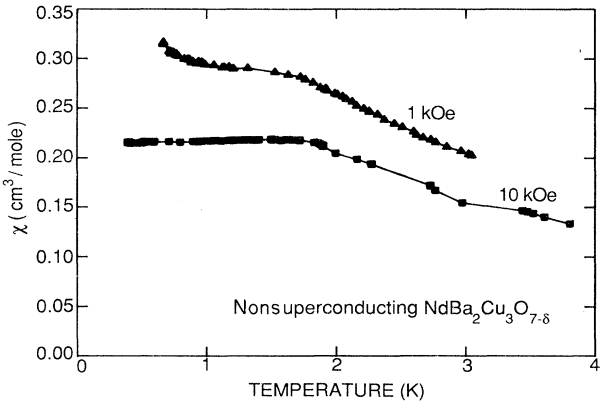

FIG. 3. Magnetic susceptibility χ ($\equiv$magnetization/applied magnetic field) in fields of 1 and 10 kOe vs temperature between ~ 0.4 and 4 K for oxygen-deficient ($\delta \approx 0.5$) nonsuperconducting $NdBa_2Cu_3O_{7-\delta}$. The breaks in slope of the χ vs temperature curves indicate antiferromagnetic order with a Néel temperature $T_N \approx 1.7$ K.

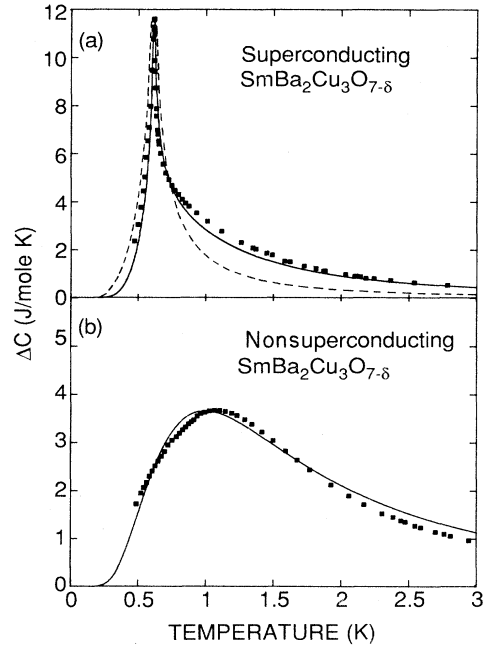

FIG. 4. Magnetic specific heat ΔC vs temperature for (a) $T_c \approx 92$ K superconducting and (b) oxygen-deficient nonsuperconducting ($\delta \approx 0.5$) $SmBa_2Cu_3O_{7-\delta}$. The solid line in (a) that has been fitted to the $\Delta C(T)$ data for $\delta \approx 0.1$ represents the solution of the two-dimensional antiferromagnetic Ising model with a Néel temperature $T_N = 0.61$ K and exchange-interaction parameters $E_1 = 0.70$ K and $E_2 = 0.063$ K. The solid line in (b) that has been fitted to the data for $\delta \approx 0.5$ represents the solution of the one-dimensional Ising model with exchange-interaction parameter $E = 1.2$ K or an electronic Schottky anomaly for a two-level system (presumably two doublets) separated by 2.4 K.

The ΔC versus T data between 0.5 and 3 K have been fitted with Eq. (7), and correspond to a ground-state doublet and an excited-state doublet at 2.38 K. The calculated curve is represented by the solid line in Fig. 4.

An alternative interpretation of the specific-heat anomaly in $SmBa_2Cu_3O_{6.5}$ can be made in terms of a 1D Ising model. The specific heat of a 1D Ising chain is given by the expression

$$C(T)=Nk_B(\beta J)^2\mathrm{sech}^2(\beta J)\ . \tag{8}$$

Equation (8) has exactly the same form as Eq. (7) for $E=2J$. A 1D Ising chain for the $SmBa_2Cu_3O_{6.5}$ sample implies an extremely anisotropic interaction ($E_1/E_2\rightarrow\infty$) in terms of the 2D Ising lattice applied to the superconducting $SmBa_2Cu_3O_{7-\delta}$ compound. Without an external perturbation such as a magnetic field, the specific-heat behavior for these two systems is identical. While the extreme anisotropy implied by the 1D Ising model appears to be physically untenable, it also seems surprising that the first excited state of the Sm^{3+} energy-level scheme would be so much lower than that in the superconducting phase, although the CEF would certainly be expected to change with increasing oxygen-vacancy concentration δ. The specific-heat feature does not change significantly in magnetic fields up to 5 kOe, which is probably due to the small magnetic moment of the Sm^{3+} ions. Specific-heat measurements in higher magnetic fields are needed to distinguish the difference between these two interpretations of the $C(T)$ data for $SmBa_2Cu_3O_{7-\delta}$.

C. Neutron scattering

Neutron scattering experiments were carried out on the $T_c\approx 92$ K superconducting phase of $NdBa_2Cu_3O_{7-\delta}$ in order to determine the magnetic structure of this compound and obtain information about the dimensionality of the magnetic ordering. Figure 5 shows two magnetic Bragg peaks found in the $\delta\approx 0.1$ compound at low temperatures. These data were obtained by subtracting[40] data taken at high temperatures from data taken well below T_N: only the magnetic contribution to the scattering will survive the subtraction procedure. The data exhibited in Fig. 5 represent a portion of a powder-diffraction pattern taken over an angular range from 1° to 65°; data taken at 2 K serve as background and have been subtracted from data taken at 60 mK, where the system is well ordered. The magnetic Bragg reflections may be indexed as $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$ reflections, respectively, on the orthorhombic chemical unit cell. The observed widths of these peaks are consistent with the instrumental resolution, thus indicating that the system exhibits 3D long-range magnetic order. Since all three Miller indices are half integer, the magnetic unit cell is just double the chemical unit cell along all three crystallographic directions as shown in Fig. 6. This is a simple magnetic structure in which nearest-neighbor spins in all three directions are aligned antiparallel, and is the same type of structure which has been found for the Gd,[28] Dy,[29,30] and Pr (Ref. 41) systems.

In addition to the basic spin configuration, which is

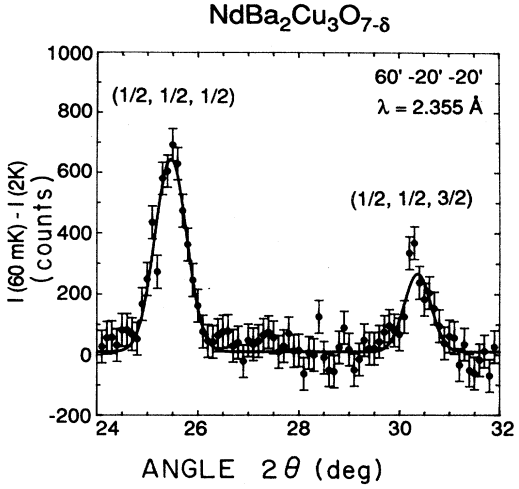

FIG. 5. Neutron scattering magnetic intensities for superconducting $NdBa_2Cu_3O_{7-\delta}$ ($\delta\approx 0.1$) at 60 mK. The two peaks may be indexed as the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$ Bragg reflections, indicating three-dimensional antiferromagnetic ordering of the Nd^{3+} ions with a magnetic unit cell which is doubled along all three cyrstallographic directions. The solid lines are least-squares fits of Gaussian peaks to the data.

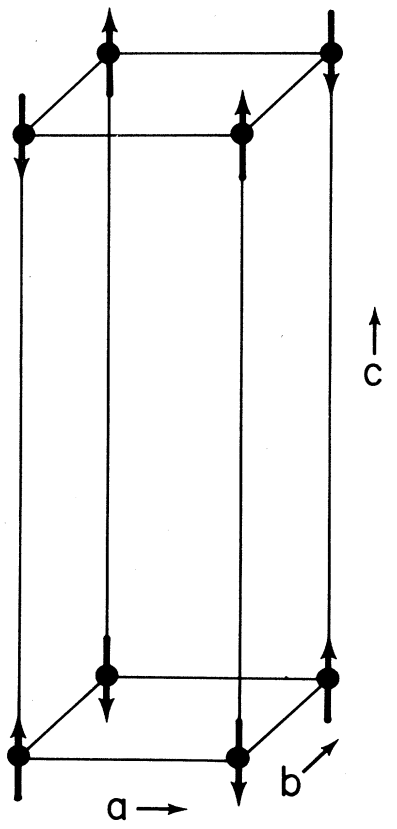

FIG. 6. Antiferromagnetic structure of the Nd^{3+} magnetic moments for superconducting ($\delta\approx 0.1$) $NdBa_2Cu_3O_{7-\delta}$.

given by the angular positions of the magnetic Bragg peaks, we can also determine the spin direction and the saturation value of the ordered (staggered) moment of the Nd. The scattering intensity for a collinear magnetic structure is given by[40,42]

$$I_M = C\left[\frac{\gamma e^2}{2mc^2}\right]^2 \langle \mu_z \rangle^2 f^2(\tau) \times \langle 1-(\hat{\tau}\cdot\hat{\mathbf{M}})^2 \rangle \frac{M_{hkl}}{\sin(\Theta)\sin(2\Theta)} , \quad (9)$$

where M_{hkl} is the multiplicity of the powder reflection, C is an instrumental constant, and 2Θ is the scattering angle for the reciprocal-lattice vector τ. The constant in the large parentheses in Eq. (9) is equal to -0.27×10^{-12} cm, $f(\tau)$ is the magnetic form factor, $\langle \mu_z \rangle$ is the thermal average of the aligned magnetic moment of the Nd ion, $\hat{\tau}$ and $\hat{\mathbf{M}}$ are unit vectors in the direction of τ and the spin direction, respectively, and the orientation factor $\langle 1-(\hat{\tau}\cdot\hat{\mathbf{M}})^2 \rangle$ must be averaged over all possible domain configurations. The considerably weaker intensity for the $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$ peak then suggests that the moment direction in the system is along the c axis, as was also found to be the case for the Gd, Dy, and Pr systems.

The only other magnetic peak that could be observed was the $(\frac{1}{2},\frac{3}{2},\frac{1}{2})$ peak as shown in Fig. 7. There are two possible peaks here, the $(\frac{3}{2},\frac{1}{2},\frac{1}{2})$ peak and the $(\frac{1}{2},\frac{3}{2},\frac{1}{2})$ peak, due to the orthorhombic symmetry. With this weak intensity, however, we could not improve the instrumental resolution sufficiently to distinguish the a and b axes. The integrated intensities for the three peaks observed are in the ratio 1:0.34(6):0.26(10) (Ref. 41) for the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$:$(\frac{1}{2},\frac{1}{2},\frac{3}{2})$:$(\frac{1}{2},\frac{3}{2},\frac{1}{2})$ peaks, respectively, while the calculated ratios assuming the moment is along the c axis are 1:0.47:0.17. The observed and calculated ratios are consistent with this assignment for the spin direction, but since there are only three observable peaks due to the small value of the magnetic moment, we should consider this spin direction determination as tentative only.

To determine the absolute value of the magnetic moment in the system, we need to ascertain the instrumental constant C, and the standard technique is to measure the intensities of several nuclear Bragg peaks.[41] The low-temperature ordered moment we obtain from our data is $\langle \mu_z \rangle = (1.07\pm0.07)\mu_B$. This value is smaller than the free-ion moment of $3.27\mu_B$ for Nd^{3+}. Crystalline electric field effects could no doubt be important in producing this small value, and inelastic neutron scattering measurements are planned to determine the crystal-field splittings in this system.

Figure 8 shows the temperature dependence of the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ peak intensity I, and reveals a typical order parameter with a Néel temperature of 0.5 K for this system. The solid curve drawn through the data is a guide to the eye. Since the intensity $I \propto M^2$ and $M \propto (T_N - T)^{\beta}$, an estimate of the critical exponent can be obtained by plotting $\ln(I)$ versus $\ln(T_N - T)$. In the range $0.6 < T/T_N < 1$, the data could be represented by a straight line, with a value of $\beta = 0.37\pm0.13$. Although the uncertainty in β is large, this value is typical for 3D long-range order. The 3D character of the AF ordering seems surprising in view of the rather good description of the specific-heat anomaly of $NdBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.1$) by the anisotropic 2D AF Ising model. Further measurements with improved sensitivity would be helpful in establishing this 3D behavior, and determining if there is a crossover from 2D to 3D character as has been observed in the $ErBa_2Cu_3O_{7-\delta}$ system.[31,32,43] Neutron scattering measurements on an oxygen-deficient $NdBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.7$) compound, which had been annealed in flowing helium gas at 800 °C, reveal an identical type of 3D AF phase transition at $T_N \approx 1.6$ K, as found in the superconducting compound at $T_N = 0.5$ K. The analysis of the

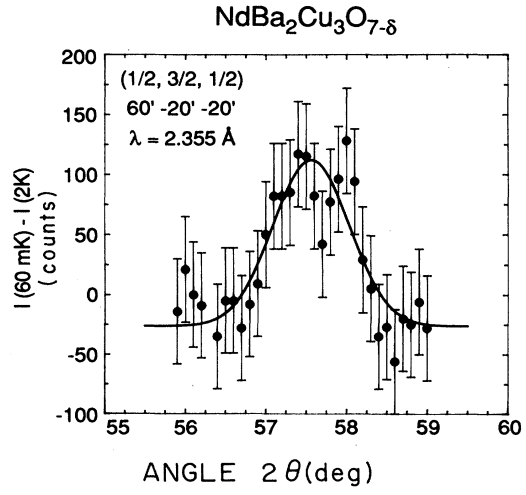

FIG. 7. The $(\frac{1}{2},\frac{3}{2},\frac{1}{2})$ magnetic Bragg peak for superconducting ($\delta \approx 0.1$) $NdBa_2Cu_3O_{7-\delta}$.

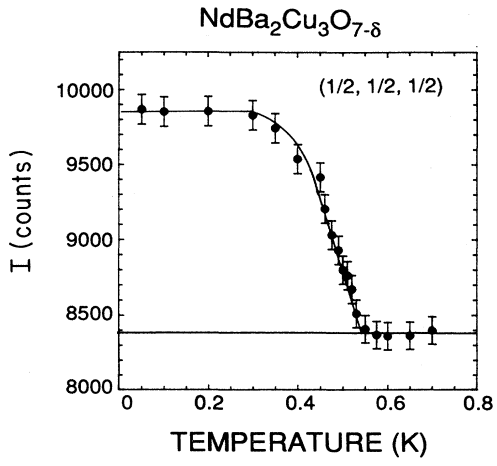

FIG. 8. Temperature dependence of the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ magnetic Bragg peak intensity, showing the square of the staggered magnetization vs temperature, for superconducting ($\delta \approx 0.1$) $NdBa_2Cu_3O_{7-\delta}$. The Néel temperature T_N is ~0.5 K for this compound.

data to obtain the ordered moment, spin direction, etc., is, however, complicated by the presence of Cu spin ordering and will be the subject of a separate study.

IV. DISCUSSION

We have shown that the specific-heat anomaly associated with antiferromagnetic ordering of the R^{3+} ions in $RBa_2Cu_3O_{7-\delta}$ compounds with R = Sm and Nd changes markedly with oxygen-vacancy concentration δ. For both superconducting $NdBa_2Cu_3O_{7-\delta}$ and $SmBa_2Cu_3O_{7-\delta}$ compounds, the specific-heat data are well represented by a 2D Ising model with an anisotropic exchange interaction in the a-b plane. An Ising model would seem to be appropriate for the $RBa_2Cu_3O_{7-\delta}$ compounds with R = Nd and Sm, since the ground states of these R^{3+} ions in the CEF are doublets.[14] Although the nonsuperconducting oxygen-deficient $NdBa_2Cu_3O_{7-\delta}$ compound also exhibits long-range antiferromagnetic ordering with an enhanced Néel temperature, we have not been able to describe the shape of the magnetic specific-heat anomaly with any models of antiferromagnetic ordering, possibly because of complications due to oxygen inhomogeneity. Preliminary low-temperature specific-heat measurements on a nonsuperconducting $NdBa_2Cu_3O_{7-\delta}$ compound ($\delta \approx 0.7$), which has been annealed in flowing helium gas at 800 °C, exhibited a sharper peak in $C(T)$ with a higher Néel temperature $T_N = 1.66 \pm 0.02$ K, in very good agreement with the neutron scattering data. An investigation of the detailed relationship between the antiferromagnetic ordering and oxygen deficiency (δ) is currently in progress. The low-temperature specific heat of the nonsuperconducting $SmBa_2Cu_3O_{7-\delta}$ compound can be described by a Schottky anomaly associated with a two-level system or by a 1D Ising chain. Neutron-diffraction measurements on the $T_c \approx 92$ K superconducting phase of $NdBa_2Cu_3O_{7-\delta}$ reveal that the Nd^{3+} magnetic moments form a simple antiferromagnetic structure in which the nearest-neighbor moments in all three dimensions are aligned antiparallel to one another along the c axis. In the $T_c \approx 92$ K superconducting phase, the ordered moment of the Nd^{3+} ions obtained from the neutron scattering data is $\langle \mu_z \rangle = (1.07 \pm 0.07)\mu_B$. The temperature dependence of the magnetic order parameter determined from the intensity of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ Bragg reflection is consistent with magnetic ordering of 3D character, in contrast to the 2D character of the excess specific heat associated with the AF order. The source of this discrepancy is not presently understood. Preliminary neutron measurements on an oxygen-deficient nonsuperconducting sample reveal the same simple antiferromagnetic structure, with a higher Néel temperature in agreement with the specific-heat results.

Several mechanisms could be involved in the long-range ordering of the R^{3+} magnetic moments in the $RBa_2Cu_3O_{7-\delta}$ compounds: dipolar, RKKY, and superexchange interactions. A number of experiments have been carried out on $GdBa_2Cu_3O_{7-\delta}$ compounds in an attempt to determine the dominant magnetic interaction. Low-temperature specific-heat measurements by Dunlap *et al.*[18] have revealed that the shape of the specific-heat anomaly associated with the antiferromagnetic ordering of the Gd ions and the value of T_N are the same for both superconducting ($\delta \approx 0.1$) and oxygen-deficient nonsuperconducting ($\delta \approx 0.85$) $GdBa_2Cu_3O_{7-\delta}$ compounds, leading these authors to conclude that the magnetic interaction in $GdBa_2Cu_3O_{7-\delta}$ is dipolar in origin. However, there is some controversy about whether or not the AF structure of $GdBa_2Cu_3O_{7-\delta}$ undergoes a subtle, but distinct change between $\delta \approx 0.1$ and 0.5. According to neutron scattering experiments on a powdered polycrystalline $GdBa_2Cu_3O_{7-\delta}$ sample with $\delta \approx 0.1$ and $T_c \approx 90$ K,[28] the Gd^{3+} spins are coupled antiferromagnetically in the a-b plane and along the c axis. However, two separate neutron scattering studies on oxygen-deficient $GdBa_2Cu_3O_{7-\delta}$ samples—a single crystal with $\delta \approx 0.5$ and $T_c \approx 40$ K (Ref. 33) and two nonsuperconducting powdered polycrystalline samples with $\delta \approx 0.6$ and 0.86 (Ref. 34)—yield different results. While the Gd^{3+} spins in both experiments are coupled antiferromagnetically in the a-b plane, the magnetic coupling between the Gd^{3+} spins along the c axis has been reported to be ferromagnetic for the single crystal with $\delta \approx 0.5$ (Ref. 33) and antiferromagnetic for the two polycrystals with $\delta \approx 0.6$ and 0.86.[34] Another difference between these two measurements is that the temperature dependence of the sublattice magnetization is consistent with 2D behavior for the $GdBa_2Cu_3O_{6.5}$ single crystal, as determined from the intensity of the $(\frac{1}{2}, \frac{1}{2}, 0)$ reflection,[33] but representative of 3D behavior for the $GdBa_2Cu_3O_{6.4}$ polycrystal, as inferred from the intensity of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ reflection.[34] It is not presently known whether this discrepancy is associated with an intrinsic difference between the magnetic structures in single and polycrystalline $GdBa_2Cu_3O_{7-\delta}$ specimens, or whether it is an experimental problem. Similar to the results reported here for $NdBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.1$), the 3D character of the antiferromagnetic ordering of the Gd^{3+} spins, determined from the neutron scattering measurements on the polycrystalline $GdBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.1$) sample, is at variance with the strong 2D Ising character inferred from the specific-heat measurements reported by van den Berg *et al.*[27]

According to Paul *et al.*,[28] calculations based on dipolar interactions alone result in a Néel temperature of only about 0.6 K for $GdBa_2Cu_3O_{7-\delta}$, which is much lower than the actual ordering temperature of 2.25 K. Moreover, dipolar interactions cannot explain the dependence of the sign of the magnetic exchange along the c axis on the oxygen occupancy revealed by the neutron scattering experiments,[28,33] nor can they produce the strong anisotropy in the magnetic coupling inferred from the specific heat of the $NdBa_2Cu_3O_{7-\delta}$ and $SmBa_2Cu_3O_{7-\delta}$ compounds, since the distances between the R^{3+} ions along the a and b axes are nearly identical. The strong dependence of the magnetic ordering temperature T_M on the oxygen-vacancy concentration δ in $NdBa_2Cu_3O_{7-\delta}$ and $SmBa_2Cu_3O_{7-\delta}$ indicates that the coupling between the R^{3+} magnetic moments involves RKKY and/or superex-

change interactions. A similar dependence of T_M on δ has also been observed by us[44] and others for[20] $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ compounds with $R=$Dy and Er through low-temperature specific-heat measurements. Evidence in favor of the RKKY interaction as the dominant mechanism for magnetic ordering in the $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ compounds is the observed scaling of the magnetic ordering temperatures T_M with the deGennes factor $(g_J-1)^2J(J+1)$ of the R^{3+} ions.[2,14,15] However, the source of the anisotropy in the exchange interaction is not readily apparent, since these materials have a rather small orthorhombic distortion and are nearly tetragonal. Thus, if the interactions between the R^{3+} magnetic moments are mediated by electrons within the adjacent CuO_2 planes between which they are situated, via RKKY or superexchange interactions, E_1 and E_2 would be expected to be comparable to one another. The most likely source of anisotropy would be the CuO chains, which are sandwiched between the CuO_2 planes and extend in the b direction. However, the CuO chains would seem to be too far away from the R^{3+} ions to produce strongly anisotropic exchange interactions which have 2D character. It is possible that the anisotropy is associated with the overlap between the Nd^{3+} doublet ground-state wave functions and valence-band states of the CuO_2 planes. Of course, one cannot rule out the possibility that the excellent description of the $C(T)$ data provided by the anisotropic AF 2D Ising model is fortuitous, and that such an interpretation is simply inappropriate.

Mössbauer isomer shift measurements on $\mathrm{GdBa_2Cu_3O_{7-\delta}}$ in the superconducting ($\delta\approx 0.1$) phase have revealed a rather small electronic charge density at the Gd nucleus,[45] indicating that conduction electrons near the Fermi level do not contribute strongly to the magnetic coupling of the Gd spins via the RKKY interaction. However, the qualitative scaling of T_M with the deGennes factor $(g_J-1)^2J(J+1)$ of the R^{3+} ions led Liu[46] to consider a modified RKKY interaction involving electrons at energies away from the Fermi level. On the basis of a simple model, it was shown that such a modified RKKY model can stabilize three-dimensional ordering of the R^{3+} magnetic moments in $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ and favors antiferromagnetism.

Note added in proof. After this paper was submitted for publication, an independent powder neutron-diffraction investigation on a $\mathrm{NdBa_2Cu_3O_{6.86}}$ sample was reported by P. Fischer, B. Schmid, P. Brüesh, F. Stucki, and P. Unternährer (Z. Phys. B **74**, 183 (1989). The results of the neutron scattering measurements on $\mathrm{NdBa_2Cu_3O_{7.8}}$ ($\delta=0.1$) describes herein are consistent with those obtained by Fischer *et al.*

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