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Long-range magnetic ordering in the high-T_c superconductors $RBa_2Cu_3O_{7-\delta}$ (R = Nd, Sm, Gd, Dy, and Er)

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Low-temperature specific-heat C measurements have been made on the high-T_c superconductors $RBa_2Cu_3O_{7-\delta}$ (R = Nd, Sm, Gd, Dy, and Er; $\delta \approx 0.1$) for $0.5 \lesssim T \lesssim 30$ K. Features in the specific heat associated with magnetic ordering of the trivalent R ions were observed for all of these compounds. The values of the magnetic ordering temperature T_M, defined as the temperature of the peak of the specific-heat anomaly due to magnetic ordering, are 0.52, 0.61, 2.25, 0.90, and 0.60 K for the compounds with R = Nd, Sm, Gd, Dy, and Er, respectively. Calculations of the magnetic entropy from the C vs T data suggest that the R ions in these compounds have doublet ground states, except for R = Gd, which has an eightfold degenerate ground state. The values of T_M for the compounds with R = Nd, Sm, Dy, and Er are in reasonable agreement with the de Gennes factor scaling of T_M for the compound with R = Gd. The de Gennes factor scaling of T_M is consistent with expectations based on the Ruderman-Kittel-Kasuya-Yosida interaction, although the agreement may be fortuitous since recent specific-heat measurements by Dunlap *et al.* on metallic and semiconducting (oxygen-deficient) $GdBa_2Cu_3O_{7-\delta}$ suggest that dipole-dipole interactions are responsible for the magnetic order in these materials.

INTRODUCTION

Following the discovery of superconductivity with a critical temperature $T_c \approx 90$ K in $YBa_2Cu_3O_{7-\delta}$,[1] the series of rare-earth (R) barium-copper-oxide compounds $RBa_2Cu_3O_{7-\delta}$ were also found to exhibit superconductivity with $T_c \approx 90$ K, except for the compound with R = La for which $T_c \approx 56$ K and the compounds with R = Ce, Pr, and Tb, which do not exhibit superconductivity above 4.2 K.[2,3] The superconducting $RBa_2Cu_3O_{7-\delta}$ compounds are isomorphic to the prototype $YBa_2Cu_3O_{7-\delta}$ compound which has an oxygen-deficient orthorhombic perovskite-type crystal structure, except for $LaBa_2Cu_3O_{7-\delta}$, which has a related tetragonal structure. Normal-state magnetic susceptibility measurements on these compounds of R elements with partially filled $4f$ electron shells revealed a Curie-Weiss-type behavior with effective magnetic moments derived from the Curie constant in good agreement with free ion values, except for the compound of R = Eu which has a nonmagnetic J = 0 ground state, as expected from Hund's rules for Eu^{3+} (Ref. 2). However, the T_c's of the $RBa_2Cu_3O_{7-\delta}$ compounds are independent of the R ion, which is surprising in view of the relatively strong effect of paramagnetic ions on the T_c of conventional superconductors.[4] This suggests that the exchange interaction between the magnetic moments of the R ions and the spins of the superconducting electrons is very weak, or alternatively, that the $RBa_2Cu_3O_{7-\delta}$ compounds exhibit an unconventional type of superconductivity that is insensitive to the presence of localized magnetic moments.[5] As part of a detailed investigation of the series of $RBa_2Cu_3O_{7-\delta}$ compounds, we have performed low-temperature specific-heat measurements on these materials between ~0.5 and 50 K. In a separate paper, we reported specific-heat data for compounds with R = Y, Eu, Ho, Tm, and Yb which revealed the absence of magnetic ordering down to ~0.5 K and the occurrence of electronic Schottky anomalies due to crystalline electric field (CEF) splitting of the energy levels of the R^{3+} ions,[6] although $HoBa_2Cu_3O_{7-\delta}$ has been reported to exhibit magnetic ordering at ~0.17 K.[7] In this paper, specific-heat data are presented for $RBa_2Cu_3O_{7-\delta}$ compounds with R = Nd, Sm, Gd, Dy, and Er which indicate that these compounds display magnetic ordering at temperatures of 0.52, 0.61, 2.25, 0.90, and 0.60 K, respectively. A brief account of the $C(T)$ data for these compounds in the vicinity of the magnetic ordering temperatures T_M was recently given in an international conference.[8] In the process of preparing this manuscript, we received several preprints reporting evidence from low-temperature specific-heat measurements of magnetic ordering for $RBa_2Cu_3O_{7-\delta}$ compounds with R = Sm,[9] Gd,[9-15] Dy,[7,9,10,14] and Er.[7,10,14]

EXPERIMENTAL DETAILS

The method in which the samples were prepared can be found in previous reports.[16] Each sample has been characterized by means of powder x-ray diffraction, electrical resistivity,[2] and low-field magnetization measurements.[16] The powder x-ray diffraction patterns for each sample consisted predominantly of lines that could be indexed to the orthorhombic perovskite-type crystal structure of the prototype compound $YBa_2Cu_3O_{7-\delta}$. The electrical resistivity data for the $RBa_2Cu_3O_{7-\delta}$ compounds studied in this work revealed superconducting transition

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temperatures with $T_c \approx 90$ K and transition widths $\Delta T_c \lesssim 2$ K.[2] Low-field (10 Oe) magnetic susceptibility measurements in the superconducting state, reported elsewhere,[16] yielded magnetic susceptibilities χ_m due to the Meissner effect and χ_s associated with induced superconducting currents, respectively. The ratio of χ_m/χ_s is between 20% and 40% for each sample, while the value of χ_s is very close to the theoretical value. The specific-heat measurements were performed in a ^{3}He semiadiabatic calorimeter at temperatures between $\sim$0.5 and 50 K using a standard heat pulse technique.

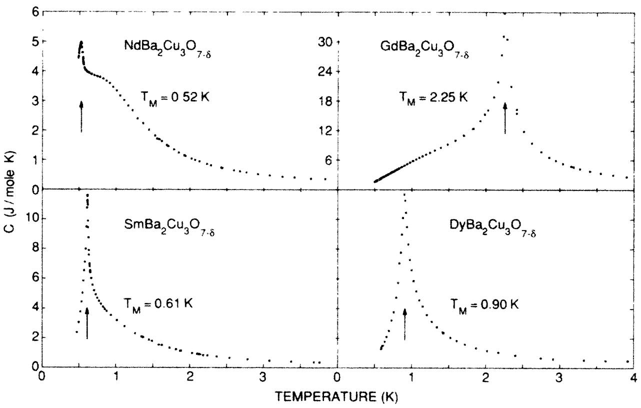

FIG. 2. Specific heat C vs temperature for $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ compounds with R = Nd, Sm, Gd, and Dy for $0.5 \lesssim T \leq 4$ K.

RESULTS AND DISCUSSION

Specific-heat C versus temperature data for $0.5 \lesssim T \leq 30$ K are shown in Fig. 1 for $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ compounds with R = Nd, Sm, Gd, Dy, and, for comparison, Y (indicated by the solid line) and in Fig. 3 for $\mathrm{ErBa_2Cu_3O_{7-\delta}}$. The anomalies in $C(T)$ due to magnetic ordering are shown in more detail in Fig. 2 for R = Nd, Sm, Gd, and Dy and in the inset of Fig. 3 for $\mathrm{ErBa_2Cu_3O_{7-\delta}}$. The transition temperature T_M defined as the temperature of the peak in the specific-heat anomaly associated with magnetic order is 0.522 ± 0.005 K for $\mathrm{NdBa_2Cu_3O_{7-\delta}}$, 0.612 ± 0.005 K for $\mathrm{SmBa_2Cu_3O_{7-\delta}}$, 2.25 ± 0.03 K for $\mathrm{GdBa_2Cu_3O_{7-\delta}}$, 0.90 ± 0.02 K for $\mathrm{DyBa_2Cu_3O_{7-\delta}}$, and 0.599 ± 0.003 K for $\mathrm{ErBa_2Cu_3O_{7-\delta}}$.

Distinct differences can be found between the magnetic specific-heat anomalies of the five compounds. The sharp specific-heat peak associated with the magnetic transition in $\mathrm{NdBa_2Cu_3O_{7-\delta}}$ is superimposed on a more rounded peak above T_M. The shapes of the specific-heat anomalies associated with the magnetic transition in the $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ compounds with R = Sm, Dy, and Er resemble those of $R\mathrm{Mo_6S_8}$, $R\mathrm{Mo_6Se_8}$, and $R\mathrm{Rh_4B_4}$ magnetic superconductors[17] in which the R ions exhibit antiferromagnetic order which coexists with superconductivity. Specific-heat measurements on $\mathrm{GdBa_2Cu_3O_{7-\delta}}$ (Ref. 15) and $\mathrm{DyBa_2Cu_3O_{7-\delta}}$ (Ref. 9) in applied magnetic fields are consistent with antiferromagnetic ordering of the R moments in these compounds. Neutron scattering measurements have revealed c-axis antiferromagnetic ordering of the Gd (Ref. 18) and Dy (Ref. 19) moments in $\mathrm{GdBa_2Cu_3O_{7-\delta}}$ and $\mathrm{DyBa_2Cu_3O_{7-\delta}}$, respectively, and a-b plane antiferromagnetic ordering of the Er moments[20] in $\mathrm{ErBa_2Cu_3O_{7-\delta}}$. The small specific-heat peak at $\sim$10.8 K in $\mathrm{DyBa_2Cu_3O_{7-\delta}}$ is probably associated with magnetic ordering in an impurity phase which we have not yet been able to identify.

Shown in Fig. 4 are entropy S versus T plots for the $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ compounds with R = Nd, Sm, Gd, Dy, and Er which were calculated using the specific-heat data according to the relation $S(T) = \int_0^T [C(T')/T']dT'$. The entropy associated with the electronic and lattice vibrational degrees of freedom was estimated from the $C(T)$ data of $\mathrm{YBa_2Cu_3O_{7-\delta}}$ (Ref. 6), and contributes less than $0.003\mathcal{R}$ ($\mathcal{R}$ is the gas constant) to the entropy and is negligible compared to the magnetic entropy. The value of the entropy $S(T_0)$ below the lower-temperature limit $T_0 \approx 0.5$ K of the specific-heat measurements was estimated from the area $C(T_0)/T_0$ of a triangle on a C/T versus T plot with vertices at 0 K, T_0, and $C(T_0)/T_0$, and

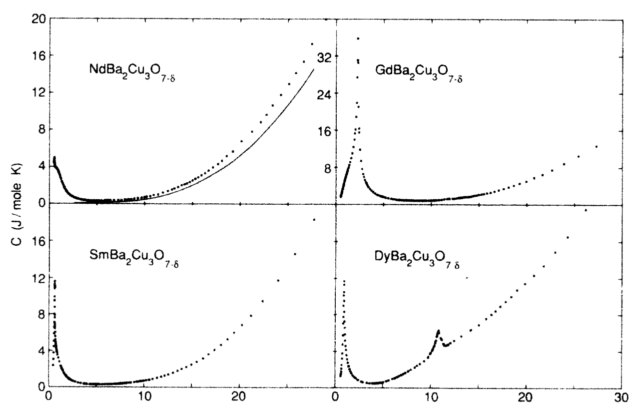

FIG. 1. Specific-heat C vs temperature for $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ compounds with R = Nd, Sm, Gd, and Dy for $0.5 \lesssim T \leq 30$ K. The behavior of $C(T)$ for $\mathrm{YBa_2Cu_3O_{7-\delta}}$ (solid line) is shown for comparison.

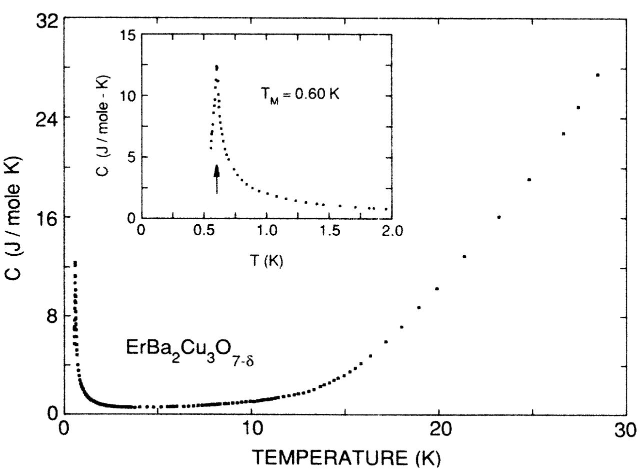

FIG. 3. Specific heat C vs temperature for $\mathrm{ErBa_2Cu_3O_{7-\delta}}$ for $0.5 \lesssim T \leq 30$ K, and $0.5 \lesssim T \leq 2$ K (inset).

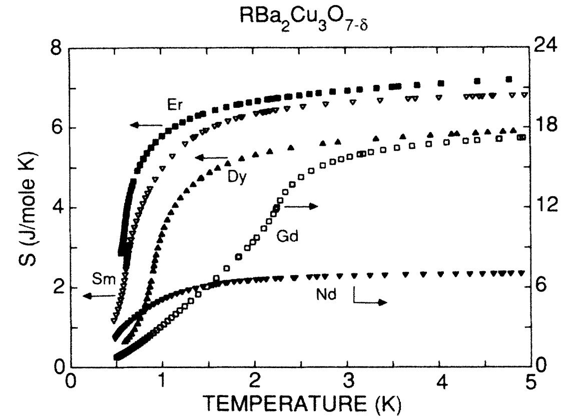

FIG. 4. Entropy S due to magnetic ordering vs temperature for $RBa_2Cu_3O_{7-\delta}$ compounds with $R=$Nd, Sm, Gd, Dy, and Er for $T\leq 5$ K. The estimation of S below the low-temperature limit $T_0\approx 0.5$ K of the specific-heat experiments is explained in the text.

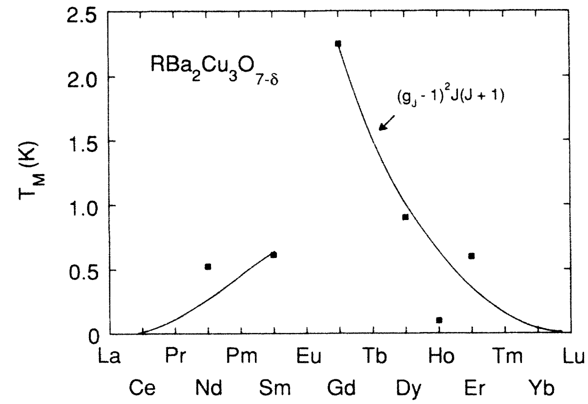

FIG. 5. Magnetic ordering temperature T_M vs R for $RBa_2Cu_3O_{7-\delta}$ compounds with $R=$Nd, Sm, Gd, Dy, and Er (this work) and Ho (Dunlap *et al.*, Ref. 7). The solid line represents the value of T_M expected from a scaling of T_M for $R=$Gd by the deGennes factor $(g_J-1)^2J(J+1)$, where g_J and J are, respectively, the Landé g factor and total angular momentum of the Hund's rules ground-state multiplet of the R^{3+} ion under consideration (after Ref. 8).

is responsible for most of the uncertainty in the calculation of $S(T)$. The values of S at T_0, T_M, and 5 K, which is well above T_M for all the $RBa_2Cu_3O_{7-\delta}$ compounds, are given in Table I. The values of S (5 K) for the compounds with $R=$Nd, Sm, Dy, and Er are close to $\mathcal{R}\ln 2=0.693\mathcal{R}$, considering the error in the estimate of S_0, which indicates that each of these compounds has a doublet ground state in the CEF. The rounded feature in the specific heat of $NdBa_2Cu_3O_{7-\delta}$ is reminiscent of a Schottky anomaly arising from a low-lying excited state produced by the splitting of the Nd^{3+} Hund's rules ground-state multiplet by the CEF. However, the entropy associated with the specific-heat anomaly up to 5 K indicates a doublet ground state for Nd^{3+} in the CEF. It is interesting to note that there are two peaks in the specific heat of another Nd compound, $NdRh_4B_4$, corresponding to two different antiferromagnetically ordered states that coexist with superconductivity in zero applied magnetic field.[21] The value of S(5 K) for $GdBa_2Cu_3O_{7-\delta}$ is very close to $\mathcal{R}\ln 8=2.08\mathcal{R}$, the value expected for the eightfold-degenerate $J=\frac{7}{2}$ Hund's rules ground state for Gd^{3+}, and indicated by low-temperature magnetization measurements on the $GdBa_2Cu_3O_{7-\delta}$ compound.[22]

The magnetic ordering temperatures T_M for the $RBa_2Cu_3O_{7-\delta}$ compounds with $R=$Nd, Sm, Gd, Dy, and Er determined from the specific-heat measurements reported here, and for $HoBa_2Cu_3O_{7-\delta}$ from recent specific-heat measurements by Dunlap *et al.*[7] are plotted in Fig. 5, which also appeared in Ref. 8. Except for $HoBa_2Cu_3O_{7-\delta}$, the variation of T_M with R conforms reasonably well to the values (solid line in Fig. 5) that have been "scaled" from the value for Gd according to the deGennes factor $(g_J-1)^2J(J+1)$, where g_J and J are, respectively, the Landé g factor and total angular momentum of the Hund's-rules ground-state multiplet of the R^{3+} ion under consideration. A deGennes factor variation of T_M with R would be expected in an isostructural series of R compounds in which the magnetic moments of the R ions are coupled by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and CEF effects are relatively unimportant. However, the agreement between the observed and deGennes scaled values of T_M may be misleading. The R ions appear to be rather well isolated from the CuO layers which are, in turn, situated between two BaO layers in the $RBa_2Cu_3O_{7-\delta}$ crystal structure, and are thought to be responsible for the superconductivity. Alp *et al.*[23] reported the results of an investigation of superconducting

TABLE I. Magnetic transition temperature T_M, magnetic entropy $S(T_0)$ at the lower-temperature limit $T_0\approx 0.5$ K, $S(T_M)$ at T_M, and S(5 K) for $RBa_2Cu_3O_{7-\delta}$ compounds with $R=$Nd, Sm, Gd, Dy, and Er.

R ion in $RBa_2Cu_3O_{7-\delta}$	T_0 (K)	T_M (K)	$S(T_0)$ ($\mathcal{R}$)	$S(T_M)$ ($\mathcal{R}$)	S(5 K) ($\mathcal{R}$)
Nd	0.484	0.522 ± 0.005	0.267	0.311	0.850
Sm	0.471	0.612 ± 0.005	0.142	0.309	0.819
Gd	0.497	2.25 ± 0.03	0.094	1.441	2.066
Dy	0.587	0.90 ± 0.02	0.077	0.289	0.711
Er	0.553	0.599 ± 0.003	0.344	0.428	0.871

$GdBa_2Cu_3O_{7-\delta}$ utilizing ^{155}Gd Mössbauer spectroscopy measurements that provide direct evidence for an absence of conduction electrons at the Gd sites in $GdBa_2Cu_3O_{7-\delta}$ and hence no interaction between the localized $4f$ electrons and the conduction electrons responsible for superconductivity. This explains why the replacement of Y ions by R ions does not reduce T_c and superconductivity coexists with the magnetically ordered states in the $RBa_2Cu_3O_{7-\delta}$ compounds with R = Nd, Sm, Gd, Dy, and Er. According to recent low-temperature specific-heat experiments by Dunlap *et al.*,[12] the feature in $C(T)$ due to magnetic ordering and the value of T_M are virtually identical for both nearly stoichiometric metallic orthorhombic and oxygen-deficient semiconducting tetragonal $GdBa_2Cu_3O_{7-\delta}$. This suggests that the magnetic ordering is not due to the RKKY interaction, which is mediated by the conduction electrons, but is rather due to dipole-dipole interactions, and perhaps even superexchange, that could be operative in metals as well as insulators. The quantitative agreement between the values of T_M and the variation predicted by the deGennes factor may be a fortuitous consequence of the effect of the reduced degeneracy of the ground states of the R^{3+} ions in the CEF on the values of T_M which are due to dipole-dipole interactions (and perhaps superexchange), rather than the RKKY interaction.

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