Low-temperature specific heat of the high-T_c superconductors $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ and $RBa_2Cu_3O_{7-\delta}$ (R=Y, Eu, Ho, Tm, and Yb)

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Low-temperature specific-heat measurements have been carried out between 0.5 and 30–50 K on the high-T_c copper oxide superconductors $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ and $RBa_2Cu_3O_{7-\delta}$ (R=Y, Eu, Ho, Tm, and Yb). The specific heat of the $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ compounds below T_c can be resolved into a contribution of the form $C_e(T)=\gamma' T$ with a finite γ' and a lattice contribution that consists of Debye and Einstein terms. Specific-heat data for the $RBa_2Cu_3O_{7-\delta}$ compounds with R=Ho, Tm, and Yb exhibit no features due to magnetic order above 0.5 K, but reveal electronic Schottky anomalies associated with crystalline electric field (CEF) splitting of the Hund's-rules ground-state multiplet of the R^{3+} ions. The Schottky anomalies can be described by calculations based on tentative energy-level schemes for the Ho^{3+}, Tm^{3+}, and Yb^{3+} ions in the CEF which are presented. Specific-heat data for the $EuBa_2Cu_3O_{7-\delta}$ compound, which can be separated into a $\gamma' T$ term, a Debye contribution, and a low-temperature upturn, are consistent with a nonmagnetic $J=0$ ground state for Eu^{3+}, as expected from Hund's rules.

I. INTRODUCTION

The recent discoveries of superconductivity with high transition temperatures T_c of $\approx$30–40 K (Refs. 1–4) in $La_{1-x}M_xCuO_{4-\delta}$ (M=Ba and Sr) and $\approx$90 K (Refs. 5–9) in $YBa_2Cu_3O_{7-\delta}$ compounds have generated a tremendous amount of research on these remarkable materials. The latter discovery also stimulated efforts to synthesize and study the isomorphic $RBa_2Cu_3O_{7-\delta}$ compounds (R=rare earth, except for Pm). Most of the $RBa_2Cu_3O_{7-\delta}$ compounds have an orthorhombic, oxygen-deficient perovskitelike structure and exhibit superconductivity with $T_c \approx 90$ K (except for compounds with R=Ce, Pr, and Tb, which are normal above 4.2 K).[10–14] $LaBa_2Cu_3O_{7-\delta}$ has a related tetragonal structure and a broad superconducting transition with an onset of $T_c \approx 70$ K,[10–14] although onsets of $T_c \approx 90$ K have been reported.[15] The insensitivity of T_c to the R ions with partially filled $4f$ electron shells and corresponding magnetic moments in these superconductors is quite contrary to what is expected in a conventional superconductor where paramagnetic ions generally produce a rapid drop in T_c.[16] This indicates that the spin-dependent exchange interaction between the R ions and superconducting electrons is very weak, or, alternatively, that these compounds display an unconventional type of superconductivity[17] that is not sensitive to the presence of paramagnetic ions. A weak exchange interaction between the R ions and the superconducting electrons is found in the ternary magnetic superconductors RMo_6S_8, RMo_6Se_8, and RRh_4B_4,[18] which display a variety of interesting phenomena associated with the interplay between long-range ordering of the R magnetic moments and superconductivity. We and others have reported that $RBa_2Cu_3O_{7-\delta}$ compounds with R=Nd,[19,20] Sm,[19–21] Gd,[19–23] Dy,[19–22,24] Ho,[24] and Er,[19–22,24] exhibit magnetic ordering at temperatures of 0.52, 0.61, 2.25, 0.90, 0.17, and 0.60 K, respectively. In this paper, we report specific-heat results for $RBa_2Cu_3O_{7-\delta}$ compounds with R=Eu, Ho, Tm, and Yb. The specific-heat data for the compounds $HoBa_2Cu_3O_{7-\delta}$, $TmBa_2Cu_3O_{7-\delta}$, and $YbBa_2Cu_3O_{7-\delta}$ do not show any magnetic transitions for $T \gtrsim 0.5$ K, but reveal electronic Schottky anomalies that arise from crystalline electric field (CEF) splitting of the rare-earth $4f$ electron energy levels. The $EuBa_2Cu_3O_{7-\delta}$ compound does not appear to exhibit any specific-heat contributions due to the magnetic moments of the R ions for $T < 30$ K, which is consistent with the nonmagnetic $J=0$ ground state of Eu^{3+} in $EuBa_2Cu_3O_{7-\delta}$ indicated by normal-state magnetic susceptibility measurements. In addition, we have also analyzed the phonon part of the specific heat of the empty $4f$ electron shell compounds $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ in terms of acoustical and optical contributions.

II. EXPERIMENTAL DETAILS

The $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ sample was prepared by chemical coprecipitation from a solution of $La(NO_3)_3$, $Sr(NO_3)_2$, and $Cu(NO_3)_2$ in the nominal molar ratio.[25] The $RBa_2Cu_3O_{7-\delta}$ samples were prepared by sintering the proper stoichiometric powder mixtures of R_2O_3, $BaCO_3$, and CuO in air at $\approx$1000 °C, followed by arc-melting in Ar to promote homogeneity, and then annealing in oxygen at $\approx$950 °C. Detailed descriptions for these two processes are given in other publications.[10,25] Sample quality and superconductive properties were characterized for each specimen by powder x-ray diffraction, electrical resistivity, and low-field magnetization measurements. The powder x-ray diffraction patterns

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exhibit major peaks of the room-temperature tetragonal perovskite-type structure for $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ and orthorhombic perovskitelike structure for the $RBa_2Cu_3O_{7-\delta}$ compounds, which are the structures for the superconducting phases. The electrical resistivity data revealed a superconducting transition at $T_c \approx 35$ K with a transition width $\Delta T_c \approx 5$ K for $La_{1.8}Sr_{0.2}CuO_{4-\delta}$,[25] and $T_c \approx 90$–94 K with $\Delta T_c \leq 2$ K for the $RBa_2Cu_3O_{7-\delta}$ compounds.[10,11] Low-field (10–20 Oe) magnetization measurements were made to determine the diamagnetic susceptibilities χ_m associated with the Meissner effect and χ_s due to induced superconducting currents. The Meissner susceptibility χ_m was obtained by measuring the susceptibility of the sample as it was cooled from the normal state to ≈ 6 K in the applied field, while the induced supercurrent susceptibility χ_s was obtained by measuring the susceptibility of the sample after it had been cooled to ≈ 6 K in zero field and the field increased to its measuring value. The ratio of χ_m/χ_s is $\approx 10\%$ to 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 ≈ 0.5 and 50 K using a standard heat-pulse technique.

III. RESULTS AND DISCUSSION

A. Specific heat of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$

Shown in Fig. 1 are specific heat C divided by temperature T vs T data for $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ for $0.5\ \text{K} \leq T \leq 50$ K. Electrical resistivity and low-field magnetization data have established that the sample is superconducting with $T_c \approx 35$ K. However, no specific-heat jump ΔC associated with the superconducting transition can be clearly delineated from the data of Fig. 1. This is probably due to two effects: (1) the small electronic specific heat $C_e(T) = \gamma T$, since $\Delta C \approx \gamma T_c$ according to the microscopic theory of superconductivity and (2) the large width of the superconducting transition which smears out the specific-heat jump. However, the slope of the C/T vs T curve changes in the vicinity of 35 K. The C/T data were linearly extrapolated to T_c both from below T_c and above T_c, and a difference $\Delta C/T_c \approx 17$ mJ/mole K^2 between the two extrapolations at T_c was obtained.[11] This value is comparable to other estimates of $\Delta C/T_c$ for $La_{1-x}Sr_xCuO_{4-\delta}$ with $x = 0.15$ and 0.2.[26]

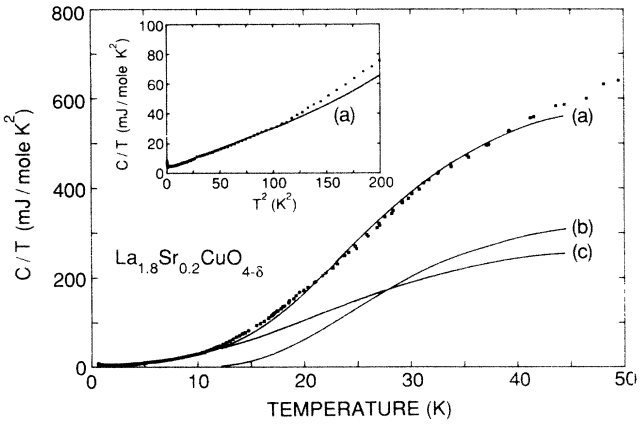

FIG. 1. Specific heat C divided by temperature T vs T for $La_{1.8}Sr_{0.2}CuO_{4-\delta}$. Inset: C/T vs T^2 for $T \leq 14$ K. The solid lines represent calculations of (a) the total specific heat in a molecular crystal model including electronic, Debye acoustic, and Einstein optical contributions, (b) Einstein optical contribution, and (c) electronic and Debye acoustic contributions.

Shown in the inset of Fig. 1 is the low-temperature C/T vs T^2 plot for $La_{1.8}Sr_{0.2}CuO_{4-\delta}$. Although the superconducting electrons should be in a condensed state and contribute an exponentially small specific heat at low temperature, a nonzero intercept on the C/T axis is evident in the figure. The low-temperature data were therefore fitted with the sum of a Debye model approximation $[C_L(T) = \beta T^3]$ for the lattice contribution and a linear term for the nonzero remanent electronic contribution $[C_e(T) = \gamma' T]$:

$$C(T) = C_e(T) + C_L(T) . \tag{1}$$

The least-squares fit of Eq. (1) to the data for $1.5\ \text{K} \leq T \leq 9$ K yields the values $\gamma' = 3.35$ mJ/mole K^2 and $\beta = 0.256$ mJ/mole K^4, the latter value corresponding to $\Theta_D = 376$ K. Similar values of γ' have been reported by other researchers.[26] Compared to the value of the electronic specific-heat coefficient γ in the normal state, which we have estimated from the specific-heat jump ΔC at T_c using the Bardeen-Cooper-Schrieffer relation $\Delta C = 1.43\gamma T_c$ to be ~ 12 mJ/mole K^2, the observed value of γ' is quite sizable. It is interesting to note that a $\gamma' T$ term was observed in our laboratory[27] 11 years ago in the specific heat below T_c of the superconducting spinel compound $Li_{1.1}Ti_{1.9}O_{3.95}$ which has a T_c of 9.6 K. A linearly temperature-dependent contribution to the specific heat in the superconducting state could be associated with a nonsuperconducting phase in the sample, or a vanishing of the superconducting energy gap over part of the Fermi surface (gapless superconductivity). Further research on higher-quality samples, with measurements to lower temperatures and in magnetic fields, will probably be required to distinguish between these two possibilities.

The specific-heat data shown in the inset of Fig. 1 deviate from the Debye approximation for $T > 10$ K, indicating the presence of higher frequency phonon branches. These higher frequency phonons were taken into account in $C(T)$ using the "molecular crystal model"[28] which has been successfully applied to the specific heat of the ternary superconductors $PbMo_6S_8$ (Ref. 29) and $LuRh_4B_4$.[30] In the $La_{2-x}Sr_xCuO_{4-\delta}$ compounds, the Cu and O ions form relatively tightly bound octahedral clusters and the entire structure can be visualized as being composed of (La,Sr) ions and CuO_6 clusters at different lattice sites. The phonon disperison curves in this compound can be simplified into two types of vibrational modes: external modes associated with vibrations of the La or Sr ions at the La sites and "rigid" CuO_6 clusters, and internal modes involving vibrations of the Cu and O atoms within the CuO_6 clusters. The external modes divide into an acoustic branch for which the Debye model is appropriate and an

optical branch which corresponds to the Einstein model. The specific heat contributed by the internal modes can be described with the Einstein model with a higher Einstein temperature than that associated with the external modes. For the $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ compounds, we have assumed three degrees of freedom for the acoustic vibrations that contribute to the Debye specific heat C_D which is given by the formula

$$C_D(T) = 3RN_D\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 e^x dx}{(e^x-1)^2}, \quad (2)$$

where $N_D = 3$ is the number of degrees of freedom, and Θ_D is the Debye temperature.

Because there is more than one characteristic optical branch in this compound, we will use one Einstein temperature Θ_E for the Einstein specific heat C_E and adjust the number of degrees of freedom for the average vibrational behavior of the optical branches; i.e.,

$$C_E(T) = N_E R\frac{x^2 e^x}{(e^x-1)^2}, \quad (3)$$

where N_E is the number of degrees of freedom, Θ_E is the Einstein temperature, and $x \equiv \Theta_E/T$. The data for 1.5 K $\leq T \leq$ 45 K were then fitted with the equation

$$C(T) = C_e(T) + C_D(T) + C_E(T), \quad (4)$$

where $C_e(T)$ is the residual linear term from the low-temperature fit to the $C(T)$ data. Since the major contribution to $C(T)$ is due to the phonons, the residual electronic term $C_e(T)$ and the superconducting jump ΔC do not affect the overall fitting. The fit yields the following values for the parameters: $\Theta_D = 196$ K, $\Theta_E = 141$ K, and $N_E R = 2.98\times10^4$ mJ/mole K which corresponds to $N_E = 3.5$. The nonintegral value of N_E indicates that the term $C_E(T)$ in Eq. (4) is an average of contributions from several optical branches characterized by different Einstein temperatures. The fitted curve which is shown in Fig. 1 and its inset, gives a good qualitative description of the $C(T)$ data. The low values of Θ_E and Θ_D indicate that the main contribution to the low-temperature specific heat is from the external modes. The detailed distribution of Einstein vibrational levels associated with the internal modes requires an investigation of the specific heat at higher temperatures.

B. Specific heat of $YBa_2Cu_3O_{7-\delta}$

Shown in Fig. 2 are C/T vs T data for 0.5 K $\leq T \leq$ 50 K for the $YBa_2Cu_3O_{7-\delta}$ compound; a plot of C/T vs T^2 at low temperature is given in the inset. The C/T vs T^2 data shown in the inset of Fig. 2 exhibit a linear behavior between 6 and 12 K and can be described by Eq. (1) with the values $\gamma' = 8.21$ mJ/mole K^2 and $\beta = 0.449$ mJ/mole K^4, corresponding to a Debye temperature of 383 K. Similar to the aforementioned results for $La_{1.8}Sr_{0.2}CuO_{4-\delta}$, the value of γ' is a significant fraction of the value of the electronic specific-heat coefficient $\gamma \approx 40$ mJ/mole K^2 in the normal state which has, for example, been estimated by Nevitt, Crabtree, and Klippert[26] from the specific-heat jump ΔC at T_c using the Bardeen-Cooper-Schrieffer relation $\Delta C = 1.43\gamma T_c$. Again, it is not known whether the $\gamma' T$ term is associated with a nonsuperconducting phase or is an intrinsic property due to the vanishing of the superconducting energy gap over a portion of the Fermi surface. The data deviate from this fit at temperatures below 6 K and above 12 K. The difference ΔC between the $C(T)$ data and the fitted curve for $T \leq 6$ K has a peak at ≈ 2 K with a maximum value of ≈ 20 mJ/mole K.[11] This deviation may be due to a magnetic impurity phase or a change of γ with T similar to that which occurs in certain heavy-fermion compounds at low temperature.[31]

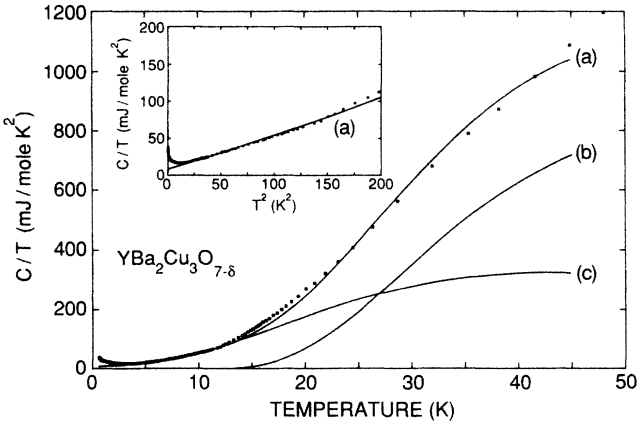

FIG. 2. Specific heat C divided by T vs T for $YBa_2Cu_3O_{7-\delta}$. Inset: C/T vs T^2 for $T \leq 14$ K. The solid lines represent calculations of (a) the total specific heat in a molecular crystal model including electronic, Debye acoustic, and Einstein optical contributions, (b) Einstein optical contribution, and (c) electronic and Debye acoustic contributions.

The high-temperature behavior for the $YBa_2Cu_3O_{7-\delta}$ compound can also be fitted with the sum of electronic, Debye, and Einstein terms [Eq. (4)]. The $C_e(T)$ term is just the $\gamma' T$ contribution discussed above and it only serves to adjust the C/T-axis intercept of the fit in Fig. 2. The values for the fit are $\Theta_D = 161$ K, $\Theta_E = 170$ K, and $N_E R = 9.45\times10^4$ mJ/mole K, corresponding to $N_E = 11.3$. The Cu-O molecular clusters of $YBa_2Cu_3O_{7-\delta}$ are much more complicated than those of $La_{1.8}Sr_{0.2}CuO_{4-\delta}$. The solid curves in Fig. 2 and its inset represent the calculated $C(T)$ curve which provides a good qualitative description of the C vs T data.

C. Specific heat of $RBa_2Cu_3O_{7-\delta}$ (R = Ho, Tm, Yb)

Shown in Fig. 3 are C vs T data for $HoBa_2Cu_3O_{7-\delta}$, $TmBa_2Cu_3O_{7-\delta}$, and $YbBa_2Cu_3O_{7-\delta}$ for 0.5 K $\leq T \leq$ 30 K, as well as $YBa_2Cu_3O_{7-\delta}$, for comparison. None of these compounds exhibits a specific-heat peak associated with magnetic ordering for $T \geq 0.5$ K. However, a calorimetrically observed magnetic transition near 0.17 K has been reported for $HoBa_2Cu_3O_{7-\delta}$ and tentatively attributed to combined nuclear-electronic ordering.[24] The

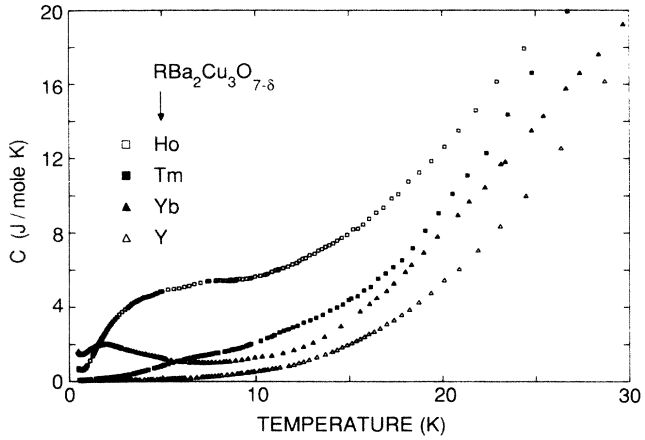

FIG. 3. Specific heat C vs temperature for $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ compounds with R = Ho, Tm, Yb, and Y.

specific heats of compounds with R = Ho, Tm, and Yb are many times larger than that of $\mathrm{YBa_2Cu_3O_{7-\delta}}$, especially at low temperature. This suggests the presence of Schottky specific-heat anomalies arising from the interaction of the R ions with the crystalline electric field (CEF). Normal-state magnetic-susceptibility measurements[11] have shown that the effective moments of the R ions in these compounds are reasonably close to the trivalent free-ion values, indicating that the $4f$ moments of the rare-earth ions are well localized. The $C(T)$ data for $\mathrm{YBa_2Cu_3O_{7-\delta}}$ are used to subtract the $C_e(T)$ and $C_L(T)$ contributions from $C(T)$ for the $R\mathrm{Ba_2Cu_3O_{7-\delta}}$ compounds with R = Ho, Tm, and Yb in order to characterize the Schottky and magnetic ordering anomalies.

Shown in Fig. 4 is the difference $\Delta C \equiv C(\mathrm{HoBa_2Cu_3O_{7-\delta}}) - C(\mathrm{YBa_2Cu_3O_{7-\delta}})$ vs T for $T \leq 25$ K. The nuclear Schottky anomaly which is commonly observed in the element Ho (Ref. 32) and many Ho compounds[33] appears to be absent in $\mathrm{HoBa_2Cu_3O_{7-\delta}}$. This indicates a very low hyperfine interaction between the Ho nuclear and $4f$ electronic moments, suggesting that the ground state of Ho is a singlet in this compound or that magnetic ordering occurs at a temperature lower than 0.5 K.

The Hund's rules ground state for Ho has a total angular momentum $J=8$, which can split into $2J+1=17$ energy levels by the CEF. The energy-level scheme that was used to calculate the Schottky anomaly (solid line) that has been fitted to the ΔC vs T data for 1.5 K $\leq T \leq$ 25 K in Fig. 4, consists of a ground-state singlet; three singlets at $\approx$ 7, 23, and 26 K; seven levels at $\approx$ 82 K; and higher levels at temperatures greater than 150 K that have a negligible effect on the low-temperature fit. It should be mentioned that the higher energy levels (i.e., $E > 26$ K) cannot be accurately determined from the low-temperature heat-capacity data. However, a singlet ground state and three low-lying singlet excited states can reproduce the broad $C(T)$ peak at $T \simeq 7.5$ K for $\mathrm{HoBa_2Cu_3O_{7-\delta}}$ quite well.

Shown in Fig. 5 are $\Delta C \equiv C(\mathrm{TmBa_2Cu_3O_{7-\delta}}) - C(\mathrm{YBa_2Cu_3O_{7-\delta}})$ vs T data for $T \leq 25$ K. A similar CEF Schottky anomaly can be observed in the tetragonal $\mathrm{TmRh_4B_4}$ compound[34] in which the CEF ground state for Tm has a degeneracy of 4. The Tm^{3+} ion has a $J=6$ Hund's rules ground state which gives a degeneracy of 13 for the free ion. The energy-level scheme for the calculated Schottky anomaly for $T \leq 20$ K consists of four states at very low temperature ($T \approx 0$ K), a singlet state at $\approx$ 17 K, three singlet states at $\approx$ 57 K, and the remaining states at energies greater than 150 K. The calculated Schottky anomaly using the levels with energies less than 60 K, is indicated in Fig. 5 by the solid curve which describes the $C(T)$ data for 4 K $\leq T \leq$ 18 K. While

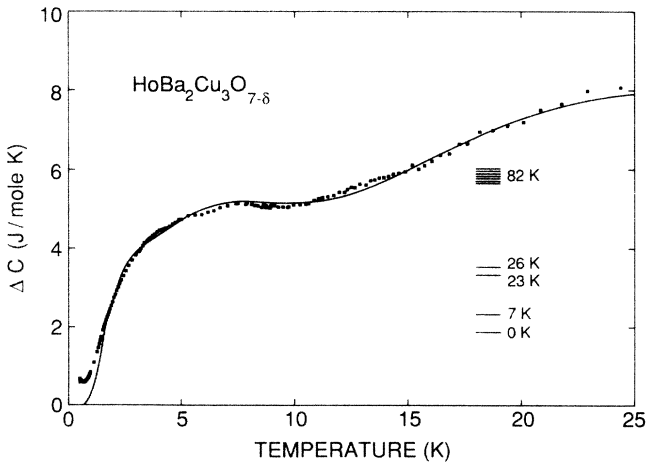

FIG. 4. Specific heat ΔC, corrected for the $\mathrm{YBa_2Cu_3O_{7-\delta}}$ background, vs temperature for the $\mathrm{HoBa_2Cu_3O_{7-\delta}}$ compound. The solid line represents the calculated electronic Schottky anomaly associated with the CEF splitting of the Ho^{3+} energy levels. The energies and degeneracies of the levels are shown in the figure.

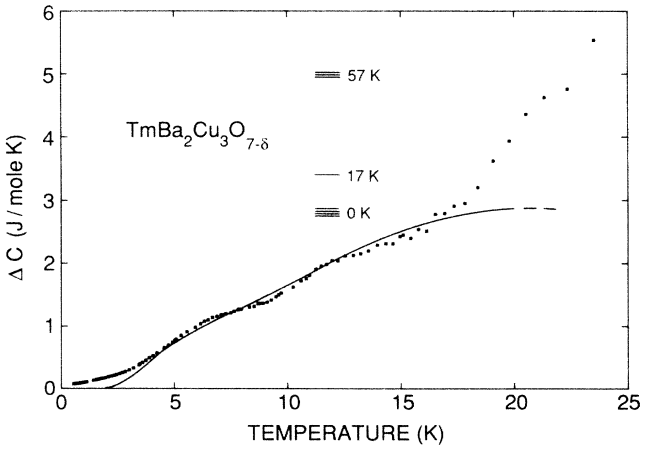

FIG. 5. Specific heat ΔC, corrected for the $\mathrm{YBa_2Cu_3O_{7-\delta}}$ background, vs temperature for the $\mathrm{TmBa_2Cu_3O_{7-\delta}}$ compound. The solid line represents the calculated electronic Schottky anomaly associated with the CEF splitting of the Tm^{3+} energy levels. The energies and degeneracies of the levels are shown in the figure.

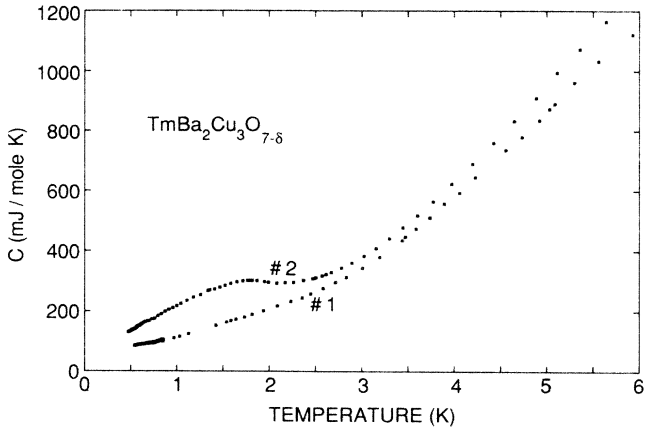

FIG. 6. Low-temperature specific heat C vs temperature data for two independently prepared $TmBa_2Cu_3O_{7-\delta}$ compounds.

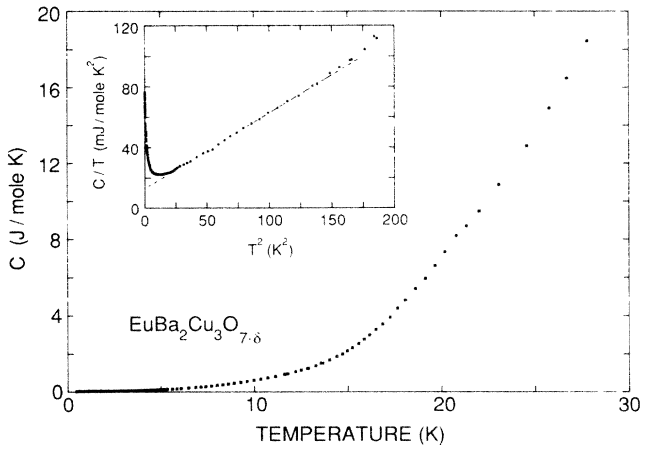

FIG. 8. Specific heat C vs temperature for $EuBa_2Cu_3O_{7-\delta}$ for $T < 30$ K. Inset: C/T vs T^2 for $T \leq 14$ K. The dashed line represents a fit of Eq. (1) in the text to the data.

higher-energy CEF levels are needed in order to yield a better fit to the data for $T > 20$ K, the origin of the discrepancy between the data and the calculated curve for $T \leq 4$ K is uncertain. However, heat-capacity data for a second sample, shown in Fig. 6 (data set 2), exhibited a small peak at $T \approx 2$ K which may indicate magnetic ordering of an impurity phase. Alternatively, the low-lying ($T \approx 0$ K) states for Tm^{3+} ions could order magnetically at very low temperature and display a high-temperature tail for $T \leq 4$ K.

Shown in Fig. 7 are $\Delta C \equiv C(YbBa_2Cu_3O_{7-\delta}) - C(YBa_2Cu_3O_{7-\delta})$ data for $T \leq 8$ K. The specific-heat feature near 2 K has a rounded peak and a more gradual decrease for $T > 2$ K, indicating a Schottky-type anomaly rather than a magnetic transition. However, the sharp upturn in ΔC for $T < 0.9$ K probably represents the high-temperature tail associated with a magnetic transition that occurs below ~ 0.5 K. Since Yb^{3+} is a Kramers ion,[35] the $J = \frac{7}{2}$ Hund's rules ground state will presumably be split into four doublets by the CEF. The ΔC vs T data between 1.5 and 8 K can be qualitatively described by a Schottky anomaly (solid line in Fig. 7) which is based on the following energy-level scheme: doublets at 0, 0.2, 4.7, and 47 K. The maximum in the calculated ΔC vs T curve is higher than the one in the experimental curve, which may be due to the presence of impurity phases (e.g., $BaCuO_2$) that reduce the amount of $YbBa_2Cu_3O_{7-\delta}$ present in the sample. Because of the upturn in the $\Delta C(T)$ data at low temperature, the energy of the lowest-lying excited state is uncertain and could lie anywhere between 0 K (i.e., a quartet ground state) and 0.2 K.

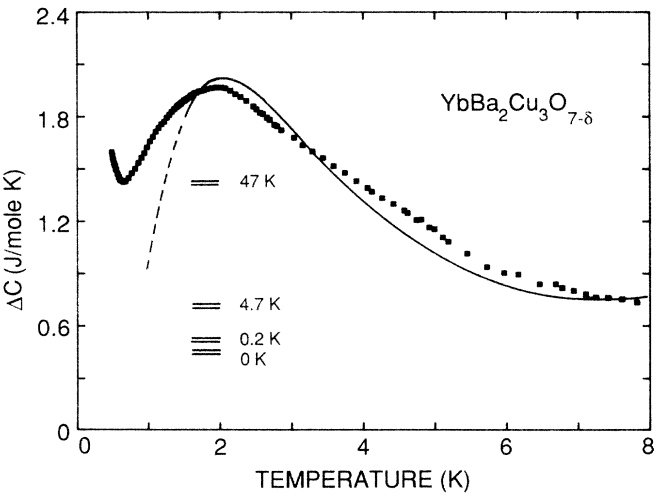

FIG. 7. Specific heat ΔC, corrected for the $YBa_2Cu_3O_{7-\delta}$ background, vs temperature for the $YbBa_2Cu_3O_{7-\delta}$ compound. The solid line represents the calculated electronic Schottky anomaly associated with the CEF splitting of the Yb^{3+} energy levels. The energies and degeneracies of the levels are shown in the figure.

D. Specific heat of $EuBa_2Cu_3O_{7-\delta}$

Displayed in Fig. 8 are C vs T data for $EuBa_2Cu_3O_{7-\delta}$ for $0.5\ \text{K} \leq T \leq 30$ K and, in the inset, C/T vs T^2 for $T^2 < 200\ \text{K}^2$. No specific-heat feature indicative of magnetic order can be observed in the $C(T)$ data which, along with normal-state susceptibility measurements,[19] are consistent with a Eu^{3+} $J = 0$ nonmagnetic ground state in this compound. The small value of the specific heat suggests contributions from conduction electrons and lattice vibrations only. Data for $T \leq 12$ K have been fitted with the sum of residual electronic and Debye model approximation terms [Eq. (1)], yielding the values for the coefficients $\gamma' = 12.9$ mJ/moleK^2 and $\beta = 0.497$ mJ/moleK^4, corresponding to a Debye temperature $\Theta_D = 370$ K. The upturn in the C/T vs T^2 data in the inset of Fig. 8 below 5 K may be due to a temperature-dependent density of states at the Fermi level or a contribution arising from a magnetic impurity phase.

IV. SUMMARY

We have measured the specific heat of the new high-T_c copper oxide superconductors $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ and

$RBa_2Cu_3O_{7-\delta}$ (R=Y, Eu, Ho, Tm, and Yb) for 0.5 K $\leq T \leq$ 50 K. The specific heat of the $La_{1.8}Sr_{0.2}CuO_{4-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ compounds below T_c can be resolved into a $\gamma' T$ contribution with a finite value of γ', and a lattice contribution consisting of Debye and Einstein terms. It is not known whether the finite γ' is an intrinsic property of the superconducting phase due to vanishing of the superconducting energy gap over a portion of the Fermi surface or an extrinsic effect arising from an impurity phase. The $RBa_2Cu_3O_{7-\delta}$ compounds with R=Eu, Ho, Tm, and Yb exhibit no specific-heat features associated with magnetic order above 0.5 K. Electronic Schottky specific-heat anomalies due to the CEF were observed in $HoBa_2Cu_3O_{7-\delta}$, $TmBa_2Cu_3O_{7-\delta}$, and $YbBa_2Cu_3O_{7-\delta}$, and a tentative energy-level scheme was proposed that yields calculated $C(T)$ curves that describe the specific-heat data for each compound. The ground state of the Ho^{3+} ion appears to be a singlet which could be responsible for the very low magnetic transition temperature and the absence of a Ho nuclear Schottky anomaly. The specific heat for $EuBa_2Cu_3O_{7-\delta}$ is comparable to that of $YBa_2Cu_3O_{7-\delta}$, indicating a nonmagnetic ground state for Eu^{3+}, as expected from Hund's rules.

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