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Specific heat and magnetic susceptibility of superconducting and semiconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

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Specific-heat (C_p) data in the range 0.4–20 K for a polycrystalline specimen of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, in the superconducting state ($\delta = 0.02$) and on the same specimen, after annealing in air, in the semiconducting state ($\delta = 0.0$), are reported. Below 10 K, C_p in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, for both $\delta = 0.02$ and 0.0, is dominated by a Schottky anomaly. The Schottky anomaly has an entropy S within 5% of the $R\ln 3$ value. Limiting values for the Debye temperature, Θ_D^0, of 409 ± 20 and 445 ± 20 K are obtained in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ for $\delta = 0.02$ and 0.0, respectively. Magnetic-susceptibility (κ) data in the range 2–280 K show that superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, undergoes a superconducting transition at 22 K. Above 40 K, κ in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, for both $\delta = 0.02$ and 0.0, exhibits Curie-Weiss behavior, which is consistent with a material that displays antiferromagnetic coupling.

I. INTRODUCTION

There is much interest in the superconducting oxides with the formula $L_{2-x}Ce_xCuO_{4-\delta}$ where L =Pr, Nd, or Sm, because the charge carriers are electrons,[1] unlike other Cu-O-plane high-T_c superconductors, e.g., $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{7-\delta}$, $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$, where the charge carriers are holes. Bulk superconductivity occurs in $Nd_{2-x}Ce_xCuO_{4-\delta}$ around $x = 0.15$ (in the range $0.14 \leq x \leq 0.18$),[1,2] and small changes in oxygen stoichiometry ($\Delta\delta \approx 0.02$) have a dramatic effect on the electrical transport properties, for example, $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$, is a superconductor with $T_c \approx 20$ K and $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.0$ is a semiconductor.[3] The structure of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ is the same as its antiferromagnetic semiconductor parent compound, Nd_2CuO_4 (T' phase), and is composed of sheets of Cu-O squares with no apical oxygen atoms. This is strikingly different from the T^*-phase structure of $La_{2-x}Sr_xCuO_4$, which displays octahedral coordination in the Cu-O planes.[1,2]

The specific heat, C_p, of superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ and $Nd_2CuO_{3.93}$ from 0.5 to 30 K have been measured by Markert *et al.*[4-6] (note the same C_p data is reported in all three references), and that of Nd_2CuO_4 by Hundley *et al.*,[7] and for both compounds it is dominated by a large anomaly below 10 K. The C_p data of Markert *et al.*[4] shows the peak of the anomaly, which is at ≈1.2 K and ≈1.7 K for superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ and $Nd_2CuO_{3.93}$, respectively, while the data of Hundley *et al.*[7] for Nd_2CuO_4 shows only the C_p upturn on the high-temperature side of the anomaly. There is evidence from neutron diffraction measurements that antiferromagnetic ordering occurs at a Néel temperature of ≈1.2 K in superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$,[8] and Markert *et al.*[4-6] and Lynn *et al.*[8] associate the C_p anomaly with the onset of this antiferromagnetic order. In contrast, a study by Boothroyd *et al.*,[9] who determined the crystalline electric field spectrum of Nd^{3+} in superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, using inelastic neutron scattering, shows that the C_p anomaly is Schottky-like. The Schottky term arises from the crystalline electric field which partially removes the $(2J+1)$-fold degeneracy of the ground state of the rare-earth ion. These neutron and C_p studies lead to the question: Is the C_p anomaly a Schottky anomaly as occurs frequently in rare-earth doped crystals, or does the anomaly have a magnetic origin, being due to the antiferromagnetic transition? The answer to this question should clarify the interesting suggestion that superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ is an example of a magnetic superconductor where superconductivity and antiferromagnetic ordering of the Nd^{3+} magnetic moments coexist.[6] There has also been a more general interest in C_p of the copper oxide based superconductors, which has included a focus on the observation that the coefficient of the linear term in C_p, γ_0, is highly variable [of order 5 mJ/(mol K^2) in $YBa_2Cu_3O_{7-\delta}$ and zero, or near zero, in $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$], and whether γ_0, or part of γ_0, is intrinsic to the superconducting state, or is extrinsic, being impurity related and/or due to some other source.[10-14]

Here we report C_p measurements in the range 0.4–20 K on a polycrystalline specimen of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ in the superconducting state ($\delta = 0.02$), and on the same specimen after heat treatment in the semiconducting state ($\delta = 0.0$). The measurement of C_p, and in particular the anomaly centered at ≈1.2 K, as function of oxygen content (to our knowledge this has not been done previously) should assist in elucidating whether the anomaly has a Schottky or magnetic character. The C_p measurements are complemented by magnetization measurements in the range 2–280 K on the same specimen, for $\delta = 0.02$ and 0.0, to determine whether any conclusions can be drawn regarding the coexistence of superconductivity and antiferromagnetic ordering in superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$.

II. SPECIMEN PREPARATION AND EXPERIMENTAL

A specimen of composition $Nd_{1.85}Ce_{0.15}CuO_4$ was synthesized via a nitrate precursor, using as primary starting materials Nd_2O_3 (99.9%), $(NH_4)_2[Ce(NO_3)_6]$ (99%), and CuO (98%). The solid nitrate mix obtained by stirred evaporation was dehydrated at 240 °C for 2 h, then decomposed and reacted by heating at 950 °C for 34 h, then at 1000 °C and 1050 °C for 14 h with intermediate regrindings. This was followed by pressing and then sintering in air at 1100 °C for 14 h. Examination of the $Nd_{1.85}Ce_{0.15}CuO_4$ specimen by x-ray diffraction showed it to be of the single T' phase. Superconductivity was induced by annealing the specimen in a nitrogen stream ($p_{O_2} \approx 2 \times 10^{-5}$ atm) for 18 h at 900 °C, and then for a further 6 h at 920 °C. Thermogravimetric measurements showed that the change from semiconducting to superconducting behavior was associated with a loss of approximately 0.02 oxygen atom per formula unit. The resultant superconducting polycrystalline $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ disk had a density of 6.21 g/cm^3, which is 85% of the crystal density. The superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ disk was cut into three specimens, one of 3.187 g for the C_p measurements, one of 0.0570 g for the magnetic measurements, and a small bar shape for electrical resistance measurements. For measurements in the semiconducting ($\delta = 0.0$) state, the same specimens were annealed in air for 12 h at 900 °C. Using these procedures it was possible to cycle repeatedly between the superconducting and semiconducting states.

The specific heat from 0.4 to 20 K was measured using a ^{3}He-^{4}He semiadiabatic heat-pulse calorimeter.[15] The accuracy of the calorimeter was determined by measuring C_p of the 1965 Calorimetry Conference copper reference material; our values agree with the measurements of Holste *et al.*[16] with an overall inaccuracy of ±0.4%. The resistance was measured using a standard four-probe dc technique in a variable temperature cryostat. Magnetization measurements were made using a variable temperature commercial SQUID magnetometer system.

III. RESULTS AND DISCUSSION

A. Resistance and magnetic measurements

Results for resistance from 1.6 to 120 K for superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$, and after annealing in air, $\delta = 0.0$, are plotted in Fig. 1. The increase in resistance with decreasing temperature shows the semiconductor character of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.0$, and of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$ above T_c. At 25 K values for the resistivity of 25.6 mΩ cm and 2.2 Ω cm are obtained for $\delta = 0.02$ and 0.0, respectively. Superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ undergoes a sharp transition to superconductivity with an onset temperature of 24.3 K and the midpoint of the transition is at 22 K.

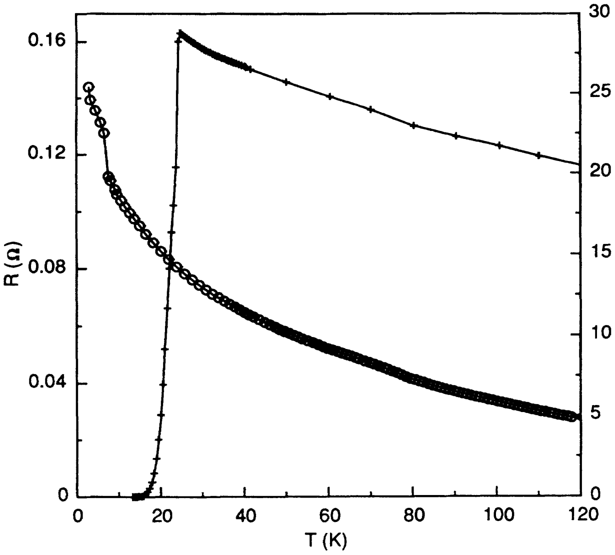

FIG. 1. Resistance R vs temperature T for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$ (+)—left-hand axis, and after annealing in air, $\delta = 0.0$ (○)—right-hand axis. The points are connected by lines as an aid to the eye.

Results for the dc magnetic rationalized volume susceptibilty (dimensionless), κ, for superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$, and after annealing in air for semiconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.0$, plotted as $1/\kappa$ versus temperature are shown in Fig. 2:

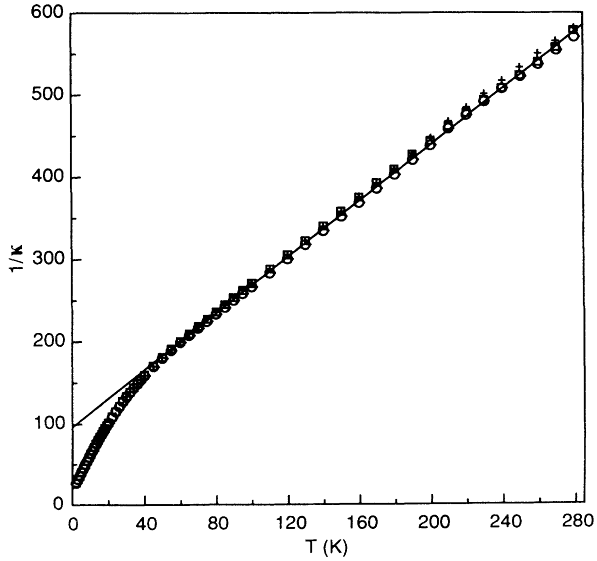

FIG. 2. Inverse magnetic rationalized volume susceptibility (dimensionless), $1/\kappa$, as a function of temperature, T for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. The symbols are defined as (+) $\delta = 0.02$ above T_c in an applied field of 0.2 T, (○) $\delta = 0.0$ in an applied field of 0.2 T, and (□) $\delta = 0.0$ in an applied field of 0.4 T. The solid curve is for a fit to a Curie-Weiss law with a Θ_C of -57.0 ± 0.5 K and a μ_{eff} of $3.67 \pm 0.05\mu_B$.

the data for $\delta = 0.0$ were taken in applied magnetic fields of 0.2 and 0.4 T in the range 2 to 280 K, while that of $\delta = 0.02$ were taken in an applied field of 0.2 T from T_c to 280 K. The magnetic susceptibility data of superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ above T_c and semiconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ are essentially identical (with perhaps the exception 220 to 280 K where the superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ data is marginally higher by about 0.5%), and above 45 K follow a Curie-Weiss law, $\kappa = C/(T + \Theta)$. This is consistent with a material that displays antiferromagnetic coupling.[17] There is deviation from a Curie-Weiss behavior below 45 K for both superconducting and semiconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. A linear least-squares fit of the magnetic susceptibility data to the Curie-Weiss law from 45 to 280 K yields a Curie-Weiss temperature Θ of -57.0 ± 0.5 K and an effective moment μ_{eff} of $(3.67 \pm 0.05)\mu_B$ for semiconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ and a Θ of (-53.7 ± 0.5) K and μ_{eff} of $(3.62 \pm 0.05)\mu_B$ for superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, compared to the Nd^{3+} free ion value for μ_{eff} of $3.62\mu_B$. The values for μ_{eff} are in good agreement with the values of $(3.56 \pm 0.05)\mu_B$ and $3.547\mu_B$ obtained in Nd_2CuO_4 (Ref. 7) and superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$,[18] respectively. With the obvious exception of superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ below T_c, the magnetic susceptibility behavior of both superconducting and semiconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ is identical, being unaffected by the oxygen content.

Below 40 K, the dc magnetization, M, for superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ was measured using two different procedures, first the specimen was cooled in zero field and a magnetic field applied with M being measured with increasing temperature from 1.9 to 40 K—denoted by ZFC, and second the magnetic field was applied when the specimen was at a temperature above T_c, typically 40 K, and M measured while it was cooled in field to 1.9 K—denoted by FC. The ZFC procedure provides an indication of M due to shielding currents and the FC procedure an indication of M due to the Meissner effect. The two procedures were repeated for applied magnetic fields of 1, 2, and 4 mT. The temperature dependence of the ZFC and FC M data are shown in Fig. 3 and a number of features are apparent; there is a well-defined superconducting transition to diamagnetic behavior, with an onset temperature of 24.3 K (in agreement with the resistance measurements); with increasing magnetic field the superconducting transition broadens; the diamagnetic moment scales linearly with the applied magnetic field; and, the ZFC data exhibit a larger diamagnetic moment than the FC data. (The ZFC data show a small "glitch" at 4 K which is not present in the FC data, and becomes more prominent with increasing magnetic field. This may be related to the granular nature of the material.) Determination of the superconducting volume fraction is not straightforward due to the effects of flux penetration of the intra- and intergranular materials. Within these limitations we estimate from the FC and ZFC data the superconducting volume fraction to be in the range 10–25% at 5 K, which seems to be typical for this compound.[19] There is no evidence of any magnetic behavior atypical of a superconductor below T_c, which might indicate the presence of a magnetic transition.

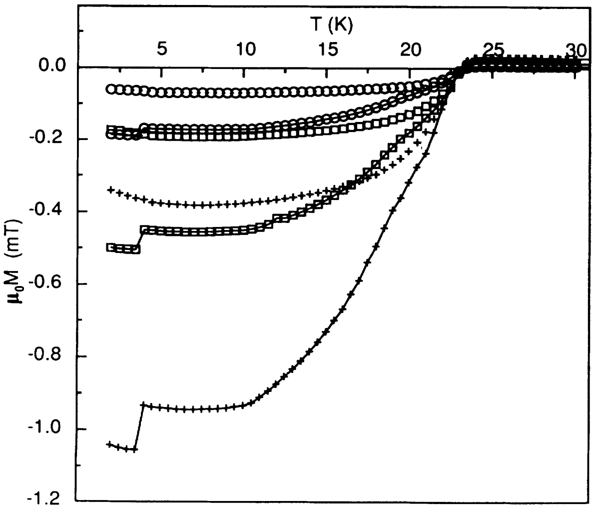

FIG. 3. Magnetization, M, of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$, in applied magnetic fields of (○) 1 mT, (□) 2 mT, and (+) 4 mT, plotted as $\mu_0 M$ vs temperature T. Zero-field cooled points are joined by a solid line while the field-cooled points are not joined by a line.

B. Specific heat measurements

Results for C_p from 0.4 to 20 K for both superconducting ($\delta = 0.02$) and semiconducting ($\delta = 0.0$) $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ are shown in Fig. 4. The overall similarity of the C_p data for both $\delta = 0.02$ and 0.0 suggests that there are no extra contributions, e.g., from a magnetic transition, to C_p for $\delta = 0.02$, when compared to C_p for $\delta = 0.0$. Also shown in Fig. 4 are the C_p data of Markert *et al.*[4] for superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, which are seen to be in good agreement with our data. Below 10 K the dominant feature is the large C_p anomaly centered at ≈1.2 K, which has a maximum value of 4.5 J/(mol K), some 1.3 J/(mol K) larger than the lattice C_p at 20 K. The C_p anomaly exhibits some sensitivity to oxygen content with its maximum value increasing by ≈7% for the change in δ from 0.02 to 0.0, but there are no changes, within experimental error, evident above 10 K where the lattice C_p dominates. Included in Fig. 4 is ΔC_p, the difference between the sets of C_p data for $\delta = 0.02$ and 0.0, determined by fitting a series of cubic splines to the $\delta = 0.02$ C_p data to generate an interpolating function, and then plotting the difference of the C_p $\delta = 0.0$ data from this function. The shape of the anomaly at ≈1.2 K is characteristic of a Schottky anomaly, as it rises rapidly on the low-temperature side, has a rounded maximum and falls slowly with a pronounced tail on the high-temperature side, whereas a C_p anomaly due to a magnetic or other cooperative transition has a characteristic λ shape, rising slowly on the low-temperature side and falling very rapidly on the high-temperature side.[20] Indeed, the shape of the C_p anomaly at ≈1.2 K in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ is quite different to the C_p anomaly observed at the Néel temperature, 5.95 K, in Sm_2CuO_4,[7] which has the characteristic shape of an anomaly due to a magnetic transition.

A Schottky anomaly occurs when the lowest energy state for an ion in a crystal is composed of two or more energy levels separated by a small energy of order k_BT. For rare-earth ions the crystalline electric field partially removes the degeneracy of the ground state; ions with half-integral ground state J values have at least a doubly degenerate ground state for a crystalline electric field of any symmetry (Kramers' theorem); and, the energy splitting is typically 1–10 K. The Schottky specific heat, $C_{\rm Sch}$, for a system of levels can be derived from[20]

$$C_{\rm Sch} = RT\frac{\partial^2(T\ln z)}{\partial T^2} = \frac{R}{T^2}\frac{\partial^2 \ln z}{\partial(1/T)^2}, \tag{1}$$

where R is the gas constant and z the partition function given by

$$z = \sum g_i \exp(-\delta_{{\rm Sch}_i}/T), \tag{2}$$

where g_i is the degeneracy of the energy level having an energy $\delta_{{\rm Sch}_i}$ in degrees K. It can be shown from Eqs. (1) and (2) for the case of a two-level system that

$$C_{\rm Sch} = R\left(\frac{\delta_{\rm Sch}}{T}\right)^2 g\frac{\exp(-\delta_{\rm Sch}/T)}{[1+g\exp(-\delta_{\rm Sch}/T)]^2}, \tag{3}$$

where $g = g_0/g_1$, and for a three-level system with g_i for all levels set equal to one

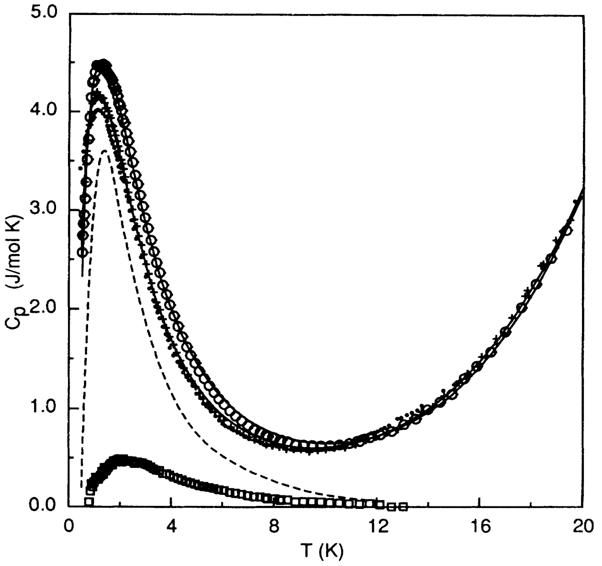

FIG. 4. C_p vs T for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$ (+), after annealing in air, $\delta = 0.0$ (○), and ΔC_p the difference between $\delta = 0.02$ and 0.0 (□). Included for comparison are the data of Markert *et al.* (Ref. 4) (●) for superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. The solid curves through the C_p data are the fitted curves to Eq. (4), with the values for the various parameters given in Table I. The calculated Schottky C_p from Boothroyd *et al.*,[9] based on parameters derived from neutron experiment, is shown by the – – – curve.

$$C_{\rm Sch} = \left(\frac{R}{T^2}\right)\left(\frac{\delta^2_{{\rm Sch}_1}\exp(-\delta_{{\rm Sch}_1}/T) + (\delta_{{\rm Sch}_1}-\delta_{{\rm Sch}_2})^2\exp[-(\delta_{{\rm Sch}_1}+\delta_{{\rm Sch}_2})/T] + \delta^2_{{\rm Sch}_2}\exp(-\delta_{{\rm Sch}_2}/T)}{[1+\exp(-\delta_{{\rm Sch}_1}/T)+\exp(-\delta_{{\rm Sch}_2}/T)]^2}\right). \tag{4}$$

It should be noted that simple Schottky theory assumes that the ions are independent of each other. The total C_p from 0.4 to 20 K of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ can be represented by the expression

$$C_p = nC_{\rm Sch} + aT^3 + bT^5, \quad {\rm J/(mol\,K)}, \tag{5}$$

where n is a measure of the ions per mol contributing to $C_{\rm Sch}$, and the T^3 term and the T^5 term account for the lattice C_p and dispersion from the acoustic mode, respectively. An Einstein term is not included in Eq. (5), to account for the effects of any low-lying optic modes, as the phonon dispersion curves for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ show that the lowest-lying optic modes have an energy of ≈150 $\rm cm^{-1}$ (216 K).[21] (The energy of the optic mode equates roughly with the Einstein temperature, $T_{\rm E}$, and typically in solids any contribution to C_p from these modes start to become evident at about $T_{\rm E}/10$, e.g., for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ above 20 K.)

The C_p data from 0.4 to 20 K for both semiconducting and superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ were fitted to Eq. (5) using a nonlinear least squares method using the $C_{\rm Sch}$ expression for a two-level system [Eq. (3)] with $g = 2$. This gave a very poor fit, in both cases the percent rms deviation of the fit was 12%, so the data were refitted to Eq. (5) using the $C_{\rm Sch}$ expression for a three-level system [Eq. (4)]. The $C_{\rm Sch}$ expression for a three-level system resulted in an excellent fit to the data for both $\delta = 0.02$ and 0.0, with a percent rms deviation of 3.1 and 3.4%, respectively. The fitted curves are included in Fig. 4, and Table I gives the values for the various parameters derived from the fit to Eq. (5), the percent rms deviation of the fit, and the limiting value for the Debye temperature, $\Theta_{\rm D}^0$, calculated from

$$\Theta_{\rm D}^0 = [(1943.73 \times N_{\rm atm})/a]^{1/3} \ \ {\rm K}, \tag{6}$$

where $N_{\rm atm} = 7$ for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. At 7.5 K there are equal contributions to the total C_p from the $C_{\rm Sch}$ high-temperature tail and the lattice C_p, and as a consequence the lattice C_p below 7 K is masked by the dominant $C_{\rm Sch}$. This results in problems in determining an accurate value for a, and hence $\Theta_{\rm D}^0$, as the fitting parameters a and b are accounting for the lattice in the presence of the large background $C_{\rm Sch}$. Values for $\Theta_{\rm D}^0$ of 409 ± 20 K and 445 ± 20 K are obtained in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, for $\delta = 0.02$ and 0.0, respectively. To ascertain if a term with a linear temperature dependence contributes to C_p, an additional term, $\gamma_0 T$, was included in Eq. (5) and the data refitted. Results from $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$,[12,14] show that at 1 K the contribution to C_p from a linear term, if present, is typically

TABLE I. Sample parameters for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$ and 0.0, derived from fitting the C_p data to Eq. (5).

δ	n	δ_{Sch1} (K)	δ_{Sch2} (K)	Θ_D^0 (K)	b [mJ/(mol K^6)]	%rms
0.02	0.9823	5.360	1.869	409	4.864×10^{-7}	3.1
0.0	1.0283	5.795	2.111	445	5.757×10^{-7}	3.4

5–10 mJ/(mol K), that is 400 times smaller than C_{Sch} in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. Clearly, in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ the very large Schottky C_p masks any linear term, making it difficult to determine its presence or abscence. At best only an estimate for γ_0 can be obtained. The result of fitting the C_p from 0.4 to 20 K for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, for both $\delta = 0.02$ and 0.0, is a marginal improvement in the percent rms deviation, small adjustments in the other fitting parameters due to the extra fitting parameter, γ_0, and a small negative value of γ_0 [-10 to -20 mJ/(mol K^2)]. We conclude that there is probably no linear term contributing to C_p, γ_0 having a value of (0 ± 10) mJ/(mol K^2).

Annealing in air the superconducting specimen of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ to render it semiconducting results in small changes of the parameters that describe the three-level Schottky term: both δ_{Sch_1} and δ_{Sch_2} increase by ≈0.4 K (7%) and n increases by ≈4%. These small changes in the Schottky term would seem to indicate that the small change in oxygen content affects the magnitude of the crystal field splittings and/or the symmetry about the rare-earth ion. Boothroyd *et al.*[9] have determined the complete crystalline electric field spectrum of Nd^{3+} in superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ from neutron inelastic scattering measurements. Their model predicts a small splitting of each of the five crystal field doublets, and the Schottky C_p calculated from their model, shown in Fig. 4, is in fair agreement with the calorimetric measurements. Although the three-level Schottky term is an excellent fit to the $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ C_p data, for both $\delta = 0.02$ and 0.0, it should be noted that this may not be a unique fit. For example, there can be variations in the shape of the Schottky anomaly due to a strong interaction between ions or strong spin-lattice coupling (Gopal[20] and references therein). We note also that a sum of two Schottky two-level terms fit the $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ C_p data, for both $\delta = 0.02$ and 0.0, just as well, though of course with an extra fitting parameter when compared to the single Schottky three-level term. The Schottky three-level term is preferred as it achieves a fit of equal quality with less fitting parameters. The dominant Schottky term at ≈1.2 K in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, for both $\delta = 0.02$ and 0.0, and its parent compound Nd_2CuO_4,[5] is unusual when compared to neodymium ethylsulphate[22] which shows no Schottky anomaly below 20 K and neodymium trichloride[23] which has a Schottky anomaly at 90 K.

The entropy, S, of the Schottky anomaly for both superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ and, after annealing in air, semiconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ was determined after first subtracting the lattice C_p ($aT^3 + bT^5$ using the parameters given in Table I) from 0.4 to 20 K. S is shown in Fig. 5 plotted as $S/(R\ln 3)$ versus temperature to highlight its convergence, within 5%, of the $R\ln 3$ value. Below 4 K S for both $\delta = 0.02$ and 0.0 is remarkably similar, though there is a subtle difference between 0.7 and 2 K where S for $\delta = 0.02$ is ≈7% larger than for $\delta = 0.0$. This difference is unlikely to be due to the lattice C_p as at 1 K it accounts for only 4.6×10^{-5} J/(mol K) of the total C_p of 4.16 J/(mol K). Above 4 K S for $\delta = 0.0$ is systematically larger than S for $\delta = 0.02$. At temperatures near 20 K the deviation from the $R\ln 3$ value is most apparent, some of which is probably due to difficulties in accurately determining the lattice C_p. The overall similarity of S for both superconducting and semiconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ would seem to preclude any extra contributions from other sources, such as entropy associated with a magnetic transition, being present in the superconducting compound but not in the semiconducting compound. It would seem that S for both $\delta = 0.02$ and 0.0 is solely due to the Schottky anomaly. On this basis there is little evidence for the coexistence of superconductivity and the occurrence of antiferromagnetic ordering at 1.2 K in superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. This does not rule out absolutely the possibility of a magnetic transition, but any entropy

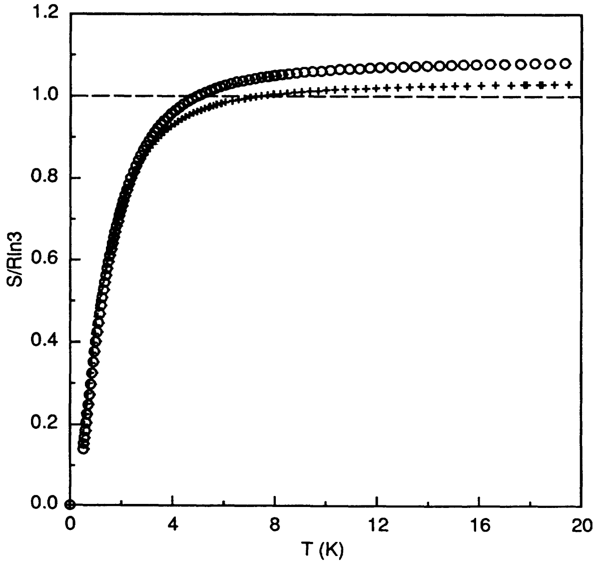

FIG. 5. Entropy, S, plotted as $S/(R\ln 3)$ vs T for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$ (+), and after annealing in air, $\delta = 0.0$ (○).

associated with it must be very small and would indicate that only a small number of ions were involved in any cooperative phenomena. It is puzzling that no entropy anomaly, and likewise no C_p anomaly, can be correlated with the neutron diffraction measurements that suggest antiferromagnetic ordering occurs at 1.2 K.[8] This puzzle may only be answered when neutron, magnetic, and C_p studies are performed on the same specimen as a function of oxygen content.

IV. CONCLUSION

The C_p measurements on the polycrystalline specimen of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$, $\delta = 0.02$, and on the same specimen after annealing in air, $\delta = 0.0$, show that the anomaly at $\approx$1.2 K has the character of a three-level Schottky system, which exhibits small changes as a function of oxygen content. The entropy of the anomaly for both $\delta = 0.02$ and 0.0 is within 5% of the $R\ln 3$ value. There are no extra contributions to C_p or S that are present when $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ is superconducting compared to when it is semiconducting that can be associated with any magnetic anomalies. Above 40 K, the magnetic susceptibility measurements for both $\delta = 0.02$ and 0.0 show a Curie-Weiss behavior, consistent with a material that displays antiferromagnetic coupling. Further neutron, magnetic, and C_p studies need to be made on the same specimen as a function of oxygen content to clarify the intriguing proposition that superconductivity and antiferromagnetic ordering coexist in superconducting $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$.

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