Heavy-Fermion-Like Excitations in Metallic $Nd_{2-y}Ce_yCuO_4$

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The specific heat of $Nd_{2-y}Ce_yCuO_4$, $0 \leq y \leq 0.2$, was measured between 35 mK and 10 K. A Schottky anomaly in Nd_2CuO_4, due to exchange interactions between Nd and Cu moments, shifts upon Ce doping to lower temperatures. In the metallic state ($y \geq 0.15$), a linear term with coefficient $\gamma \simeq 4\,J/K^2$ per mole Nd is found below 300 mK. For $y = 0.2$, a constant value of the magnetic susceptibility in the same temperature range and changes of C_p in applied magnetic fields suggest an interpretation in analogy to a heavy-fermion system resulting from the coupling between Nd moments and conduction electrons.

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In many superconducting cuprates containing magnetic rare earths, coexistence of superconductivity and antiferromagnetic order of rare-earth moments at low temperatures has been found [1–4]. In compounds of the type $RBa_2Cu_3O_7$, R = Nd, Gd, Er, ..., the sites of both Cu and O atoms in the CuO_2 planes in which the carriers of supercurrents are located have symmetrical positions with respect to rare-earth moments of opposite directions. Hence, magnetic fields arising from ordered rare-earth moments cancel at these Cu and O sites and do not adversely affect superconductivity.

The situation is quite different in La_2CuO_4, a compound with T structure and in R_2CuO_4, R = Pr, Nd, Sm, Eu with T' structure. In these cuprates, the sites of Cu and O atoms in CuO_2 planes are in symmetrical positions with respect to pairs of oppositely directed *nearest-neighbor* rare-earth moments only. However, magnetic coupling is possible between Cu and moments of next-nearest rare-earth neighbors at a distance of 4.75 Å in La_2CuO_4 and 4.26 Å in Nd_2CuO_4, in a direction parallel to the crystallographic c axis. This is irrelevant in $La_{2-y}Sr_yCuO_4$ since La is nonmagnetic. However, when magnetic Gd [5] or Nd [6] is substituted for La in $La_{1.85}Sr_{0.15}CuO_4$, T_c decreases rapidly.

In the cuprates R_2CuO_4 with T' structure, $Eu^{3+}(J = 0)$ is nonmagnetic, and the crystal-field ground state of Pr^{3+} is a nonmagnetic singlet. The other rare-earth ions, Nd^{3+}, Sm^{3+}, and Gd^{3+}, all carry magnetic moments. Clear evidence for exchange interactions between rare-earth and copper moments in Gd_2CuO_4, Pr_2CuO_4, and Nd_2CuO_4 has been derived from several experimental studies [3,7–9].

In Nd_2CuO_4, first evidence for Cu-induced ordering of Nd moments was obtained by magnetic neutron diffraction [3]. In addition, magnetic splitting of the Nd crystal-field doublets due to Nd-Cu exchange interactions was inferred from a study by inelastic neutron scattering [7] of crystal-field splitting of the Nd $4f$ state. These authors pointed to the similarity of the low-temperature anomaly in the specific heat C_p of Nd_2CuO_4 with a Schottky anomaly. This interpretation of the C_p anomaly was fully confirmed by a quantitative analysis of the results obtained by measurements in zero applied field and in an applied field of 4.4 T [8]. Furthermore, the temperature dependence of neutron diffraction peaks whose intensity is determined by the Nd moments [3,9] is reproduced by this assumption [8].

This interpretation of the C_p anomaly in Nd_2CuO_4 is entirely based on the presence of static copper moments due to their antiferromagnetic order below $T_N^{Cu} \simeq 270$ K. Thus, a drastic change of the specific heat is expected for doped and reduced compounds $Nd_{2-y}Ce_yCuO_4$ for doping levels $y \gtrsim 0.14$ in which copper moments do not order [10]. Yet, measurements of the specific heat of $Nd_{1.85}Ce_{0.15}CuO_4$ yielded an anomaly whose essential features are quite similar to the anomaly observed in the undoped compound [11].

In order to clarify these highly surprising observations we have begun a systematic study of the low-temperature specific heat of doped compounds $Nd_{2-y}Ce_yCuO_4$ as a function of the Ce content y.

Samples were prepared by standard ceramic techniques. Appropriate oxide mixtures were thoroughly ground and subjected to a series of heat treatments in the temperature range 900 to 950 °C in air, with intermediate regrinding procedures. A final sintering step at 1050 to 1100 °C was followed by reduction treatments between 900 and 950 °C in N_2 or in Ar. The Ce contents were $y = 0, 0.1, 0.15$, and 0.2, respectively. Structural parameters and phase purity (with a sensitivity of about 2%) were determined by x-ray diffraction. The metallic character of the overdoped ($y = 0.2$) sample was verified by measurement of the resistance in the temperature range from 4 to 300 K. For the Ce content $y = 0.15$, the specific heat of three different samples was measured. Sample A was not reduced, the electrical resistance showed semiconducting character, and no transition to the superconducting state was found. For samples B and C, different sequences of annealing treatments were chosen. In both samples, measurements of the dc susceptibility

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with a SQUID magnetometer showed the occurrence of a superconducting transition at $T_c \simeq 20$ K. However, the Meissner (MF) and shielding (SF) fractions of the two samples were quite different: For sample B (reduced at 925 °C in N_2), we obtained MF = 23% and SF = 29%, whereas for sample C (reduced in two steps, 6 h at 950 °C, then 15 h at 900 °C, also in N_2), MF = 30% and SF = 72%.

The specific heat was measured with semiadiabatic heat-pulse calorimeters, in a dilution refrigerator for the temperature range 35 mK $\lesssim T \lesssim$ 3 K, and in a He-bath cryostat for temperatures from 2 K to about 10 K. Specific-heat measurements were carried out in zero field and in applied magnetic fields up to 4 T.

The specific heat $C_p(T)$ of all samples measured in zero field is displayed in Fig. 1(a). The data shown for Nd_2CuO_4 and for $Nd_{1.9}Ce_{0.1}CuO_4$ have been corrected for a nuclear term $\alpha_{\rm nuc}T^{-2}$. In the case of Nd_2CuO_4, the value of the coefficient $\alpha_{\rm nuc}$ which agrees with the experimental results corresponds to a hyperfine field of about 170 T at Nd nuclei, in good agreement with the field expected for $\mu_{\rm Nd} \simeq 1.3\,\mu_B$ [9]. In $Nd_{1.9}Ce_{0.1}CuO_4$, the field is reduced to about 160 T. For compounds with higher Ce content, an upturn of the zero-field results is also found at the lowest temperatures. However, it was impossible to describe this upturn by either a T^{-2} or a T^{-1} term. For these compounds, plots of C_pT^2 versus T^3 yield crude estimates for the values of $\alpha_{\rm nuc}$ in the range (2 to 5)$\times 10^{-4}$ JK/mole. The uncertainties are large since these plots are not really linear. The resulting reductions of $\gamma(T) = C_p(T)/T$ amount at most to 10% of the values appearing in Figs. 1(b), 2(b), and 3(b) which show uncorrected data.

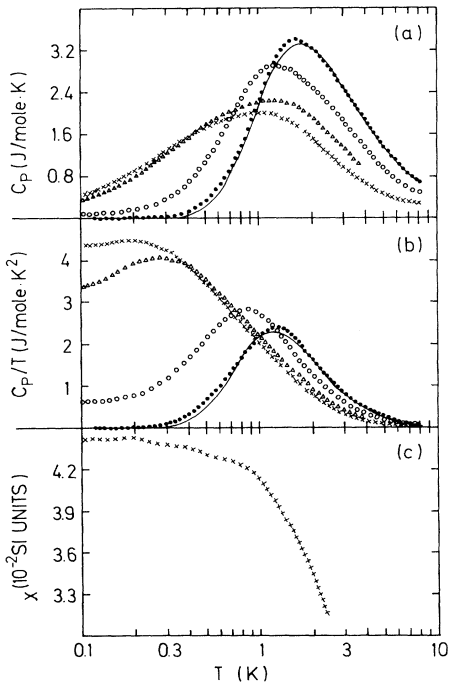

FIG. 1. (a) Zero-field specific heat $C_p(T)$ per mole Nd and (b) $C_p(T)/T$ of compounds $Nd_{2-y}Ce_yCuO_4$: (•) $y = 0$, (○) $y = 0.1$, (△) $y = 0.15$ (sample C), (×) $y = 0.2$; (c) ac susceptibility $\chi(T)$ of $Nd_{1.8}Ce_{0.2}CuO_4$.

In agreement with results reported earlier [8,11], the data for Nd_2CuO_4 correspond quite well to a Schottky anomaly modified by Nd-Nd exchange interactions [continuous line in Fig. 1(a)]. For Ce-doped samples, the anomaly rapidly changes its character, particularly between Ce content $y = 0.1$ and $y = 0.15$, that is, with the transition from the semiconducting to the metallic phase. A remarkable feature of the low-temperature data for Ce-doped compounds is a linear term which increases drastically from $y = 0.1$ to $y = 0.15$. This is clearly seen in Fig. 1(b) showing values of $\gamma(T) = C_p(T)/T$. For the overdoped compound $Nd_{1.8}Ce_{0.2}CuO_4$, the very large value $\gamma \simeq 4.4$ J/mole K^2 is obtained in the low-temperature limit. The results for metallic compounds ($y = 0.15, 0.2$) are very similar to those generally observed in heavy-fermion systems [12]. Calculations of the specific heat with the resonant-level model [13] have only led to qualitative agreement with our experimental data. These calculations yield estimates for the characteristic temperature T^* associated with the anomalies for the metallic compounds $Nd_{2-y}Ce_yCuO_4$ in the range 1 to 2 K. For $Nd_{1.8}Ce_{0.2}CuO_4$, the analogy with heavy-fermion systems is strongly underlined by the magnetic susceptibility, measured inductively at a frequency of 105 Hz. The result is displayed in Fig. 1(c). Below about 0.4 K, the susceptibility saturates near a value of 0.044 SI units ($\simeq 0.11$ emu per mole Nd). With $\mu_{\rm Nd} = g_{\rm Nd}s\mu_B$ where $s = \frac{1}{2}$, the low-temperature results for γ and χ yield for the Sommerfeld-Wilson ratio:

$$R = \frac{4\pi^2 k_B^2}{3g_{\rm Nd}^2\mu_B^2}\frac{\chi}{\gamma} = \frac{8.0}{g_{\rm Nd}^2}. \qquad (1)$$

An estimate for the value of $g_{\rm Nd}$ which is appropriate for our susceptibility measurements on polycrystalline material can be derived from the ordered moment in Nd_2CuO_4 (parallel to the Cu-O_2 planes), $2\mu_{\rm Nd} = g_\parallel\mu_B \simeq 2.6\,\mu_B$ [9], together with single-crystal data for the magnetic susceptibility of Nd_2CuO_4 [14], yielding $(g_\parallel/g_\perp)^2 = \chi_\parallel/\chi_\perp \simeq 4$. These values are hardly affected by Ce doping [15]. Thus, with $\langle g_{\rm Nd}^2\rangle = (2g_\parallel^2 + g_\perp^2)/3 \simeq 5.1$, we obtain $R = 1.6$, in agreement with theoretical predictions for heavy-fermion systems [16].

Another similarity with heavy-fermion systems is the influence of a magnetic field upon the specific heat [12,17]. As illustrated in Fig. 2 for $Nd_{1.8}Ce_{0.2}CuO_2$, a field of 2 T hardly affects the specific heat. However, in higher fields, $\gamma(T)$ drops precipitously to small values. In high fields, the temperature dependence of C_p approaches the shape of a Schottky anomaly. Also, the low-temperature upturn in fields of 3 and 4 T is well de-

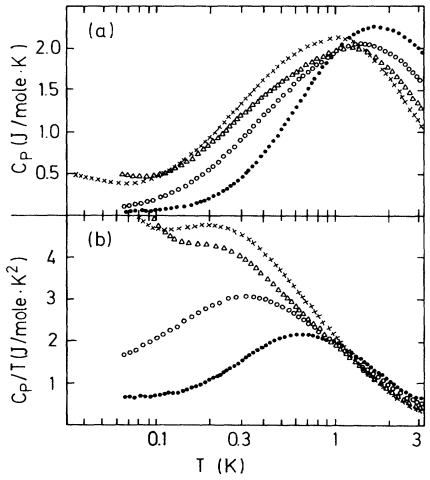

FIG. 2. (a) Specific heat $C_p(T)$ per mole Nd and (b) $C_p(T)/T$ of $Nd_{1.8}Ce_{0.2}CuO_4$ in magnetic fields B_{appl}: (x) $B_{appl} = 0$, (△) $B_{appl} = 2$ T, (○) $B_{appl} = 3$ T, (•) $B_{appl} = 4$ T.

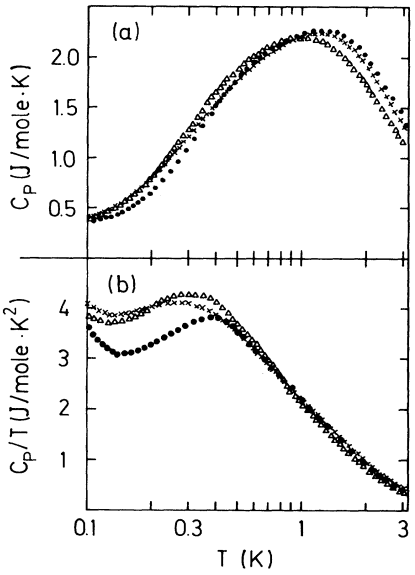

FIG. 3. (a) Specific heat $C_p(T)$ per mole Nd and (b) $C_p(T)/T$ of different samples $Nd_{1.85}Ce_{0.15}CuO_4$: (•) sample A (not reduced), (△) sample B, (x) sample C; the difference between samples B and C is discussed in the text.

scribed by a nuclear T^{-2} term, which is not true for the results obtained in fields 0 and 2 T. These results provide another measure for the characteristic energy scale of the excitations giving rise to the anomaly of the specific heat as the interaction between an external field of 4 T and the Nd moments obviously is stronger than the internal interactions. If the Nd moments are near $1\,\mu_B$, this corresponds to a temperature of about 3 K, near the value of T^*, derived from the calculations with the resonance-level model. Similar results were obtained for the specific heat of $Nd_{1.85}Ce_{0.15}CuO_4$ in applied fields.

In Fig. 3, zero-field results for the three samples $Nd_{1.85}Ce_{0.15}CuO_4$ are compared. These data were not corrected for nuclear contributions since the low-temperature upturn is not described by a T^{-2} term. Obviously, the low-temperature limit of γ is significantly smaller for the nonreduced sample A than for the superconducting samples B and C. The bulge near 0.4 to 0.5 K in the data for sample B (with the smaller fraction of superconducting material) indicates the presence of a contribution with Schottky-like character in this sample. This feature may well be an indication for the existence of antiferromagnetically ordered regions as they have been revealed in $Nd_{1.85}Ce_{0.15}CuO_4$ by NMR studies [18,19]. According to results reported by Kambe *et al.* [19], such regions exist in partly oxidized materials, whereas the corresponding zero-field signal has not been observed in thoroughly reduced samples [19,20]. In addition, phase separation, found in $Nd_{2-y}Ce_yCuO_4$ near $y = 0.15$ [21], may also play a role. We have no quantitative evidence concerning the fraction of antiferromagnetic material in our samples. However, the susceptibility data indicate that the superconducting, nonmagnetic fraction is largest in sample C. Thus, the specific heat of this sample should be closest to that of a fully superconducting compound.

In all cases, the entropy associated with the anomaly approaches $R\ln 2$ at 8 K. Larger values are obtained when nuclear contributions are not subtracted.

The total ensemble of our experimental results clearly proves the persistence of Nd-Cu exchange coupling in $Nd_{2-y}Ce_yCuO_4$ for all Ce concentrations $0 \leq y \leq 0.2$, in good agreement with concurrent evidence derived from ^{63}Cu NMR: Characteristic changes of the Knight shift and of the resonance linewidth occurring in the temperature range of the specific-heat anomaly indicate the presence of Nd-Cu exchange interactions [18,20].

In the undoped compound and for Ce contents $y \lesssim 0.14$, Cu moments are mostly static in the temperature range in which the Nd-Cu interaction becomes effective since the ordering temperature of the Cu moments is quite high. Thus, the low-temperature anomaly of the specific heat essentially has the character of a Schottky anomaly. With Ce doping, additional electrons which have predominantly Cu $3d$ character [22] are introduced. The magnetic moment of a Cu atom occupied by one of these electrons vanishes, and consequently its exchange coupling with two Nd moments. This implies a net reduction of the Nd-Cu coupling strength by Ce doping. In addition, the electrons are not localized at a single Cu site. For low Ce content, $y \lesssim 0.14$, they appear to be localized in small regions comprising a few Cu sites, presumably in the vicinity of Ce impurities [23]. Thus, Nd moments in the neighborhood of these regions experience fluctuating exchange fields. This may well contribute to the shift of the specific-heat anomaly towards lower temperatures. Furthermore, the transfer of an electron from

one Cu site to another is affected by the fact that the transfer involves the decoupling of two Nd moments from the Cu moment at that site.

With the transition to the metallic state for Ce content $y > 0.14$, that is, when the added electrons become itinerant, the combination of the intimate coupling of Nd moments to moments at Cu sites which are not occupied by conduction electrons and of Nd-Nd interactions appears to lead to a state which bears strong resemblance to a heavy-fermion system.

Obviously, this is also true for superconducting $Nd_{1.85}Ce_{0.15}CuO_4$. Note that the behavior in this compound is completely different from that of typical heavy-fermion *superconductors* [12]. There, the transition to superconductivity occurs at very low temperatures, and the heavy quasiparticles are carriers of the supercurrents. In $Nd_{1.85}Ce_{0.15}CuO_4$, in contrast, the transition to the superconducting state occurs at a temperature well above the formation of the quasi-heavy-fermion state. According to a theoretical model by Fulde *et al.* [24], the heavy-fermion system in Ce-doped Nd_2CuO_4 is a new prototype resulting from the interaction of the Nd moments with the *strongly correlated* conduction electrons at Cu sites, whereas in classical heavy-fermion systems f moments are coupled to conduction electrons for which correlations are negligible. In contrast to the classical case where mainly conduction electrons with energy close to E_F participate in the singlet formation, most of the conduction electrons are involved in the case of strongly correlated conduction electrons. Consequently, the very weak coupling between Nd spins and Cu d electrons leads to appreciable effects even in the metallic state although the corresponding Kondo temperature in the conventional picture would be practically zero. Presumably, also compounds $R_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, cuprates for which large values of γ up to more than 200 mJ/moleK^2 have been reported for the first time [25], belong to the new type of heavy-fermion systems.

An alternative interpretation of the large linear terms in the specific heat could be sought in a wide distribution of localized magnetic excitations resulting from disorder. Such effects have been observed in amorphous rare-earth alloys [26], but the largest values of γ ever found in systems of this type are of order 100 mJ/moleK^2. Furthermore, the observed temperature dependence of the magnetic susceptibility of $Nd_{1.8}Ce_{0.2}CuO_4$ is in strong contrast to that observed for amorphous alloys, thus strongly favoring the interpretation of our results in analogy to heavy-fermion systems.

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