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LOW TEMPERATURE SPECIFIC HEAT IN SUPERCONDUCTOR $Nd_{2-y}Ce_yCuO_4$

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The large low-temperature specific heat in $Nd_{2-y}Ce_yCuO_4$ has been explained as caused by the localized many-electron low-energy excitations of the Nd^{3+} ions. These excitations are associated with the formation of two-closely lying localized states, with a gap $\delta_K <$ 0.5 meV, originating from the charge-formed Kramers doublet ground state. With the Ce substitutions the energy splitting decreases resulting in shifting of the Schottky-like specific heat to ultra-low temperatures. Copyright © 1996 Elsevier Science Ltd

1. INTRODUCTION

The Ce-doped Nd_2CuO_4 system exhibits superconductivity (SC) with the maximum SC-temperature of 24 K for the compound with 0.15 Ce substitution. This superconductivity is of the electron-type as it is believed that one extra electron is brought to the system by the Ce ion provided its tetravalent state. The existence of the superconductivity in this system, compared with the Sr-doped La_2CuO_4 system, is taken as the confirmation of the electron–hole symmetry in the formation of the superconductivity, at least in this class of materials. The system $Nd_{2-y}Ce_yCuO_4$ attracted much interest after the observation of the large ultra-low temperature specific heat for the compound with $y = 0.15$ and 0.2 [1]. The experimental data are shown in Fig. 1. The derived Sommerfeld coefficient γ of $\sim 4.4\,J\,K^{-2}$ mole Nd is enormous as it is nearly three times bigger than the observed one for the heaviest heavy-fermion system $CeAl_3$[2].

The maternal system Nd_2CuO_4 exhibits strong magnetic correlations that produce antiferromagnetic structure below 260 K due to the Cu-ion spins. Magnetic ordering of the Nd-ion spins takes place below helium temperature only [3]. The multiplet structure of the Nd ions has been ambiguously proved to exist by inelastic-neutron-scattering (INS) studies [4–8].

The aim of this paper is to study the physical origin of the large low-temperature specific heat in the Ce-doped Nd_2CuO_4 system. Attention is given to many-electron states of the trivalent Nd ions and, in particular, to the appearance of the two closely-lying localized states due to the removal of the Kramers degeneracy of the charge-formed Kramers doublet ground state.

2. THE FINE ELECTRONIC STRUCTURE (FES) OF THE Nd^{3+} IONS

The Nd^{3+} ion consists of 3f electrons. Their orbital and spin movements are highly correlated such that the total angular momentum **J** becomes the good-quantum number. A 4f ion, when placed in a solid, experiences the electric-field potential. As an effect of this potential the degeneracy is lifted and different charge-formed (CF) ground states of the f subsystem are realized [9–11]. For the Nd^{3+} ion the lowest multiplet given by Hund's rules is $^4I_{9/2}$ with $J = 9/2$, $S = 3/2$, $L = 6$ and the Landé factor $g = 8/11$. The 10-fold $(= 2J + 1)$ degenerate ground multiplet $|LSJ>$ is split, with respect to the J_z component, by the crystal-line-electric-field (CEF) interactions of the tetragonal symmetry in the form

$$H_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4 \qquad (1)$$

into five Kramers doublets. So, the fine electronic structure (FES) of the Nd^{3+} ion contains five Kramers
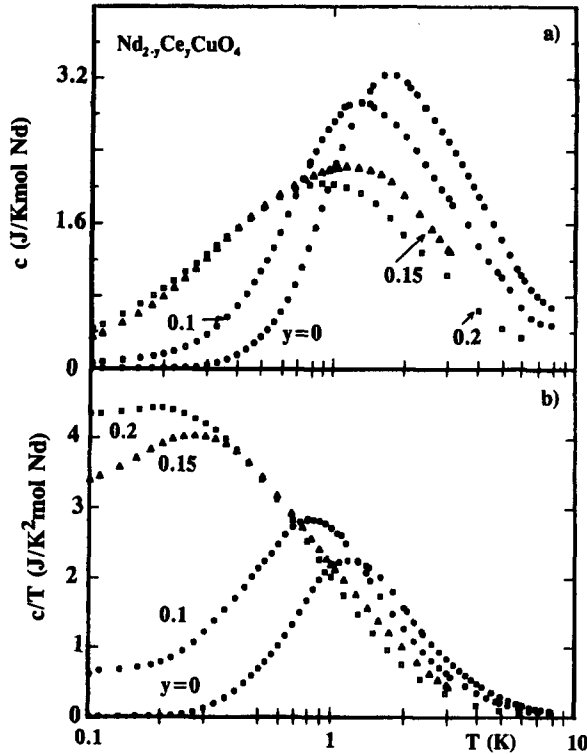
Fig.1. The experimental temperature dependence of the specific heat for $Nd_{2-y}Ce_yCuO_4$ compounds, after [1]. The data refer to the mol of Nd ions. For $y = 0.15$ and 0.20 the specific heat at low temperatures is very large and mimics behaviour observed for heavy-fermion intermetallic compounds.

doublets. Their symmetries and energetical positions are the subject of theoretical and experimental studies. The tetragonal terms B_4^4 and B_6^4 cause the mixing of the $|LSJJ_z >$ states with J_z values different by ± 4. As a result, the atomic-like states $\pm 5/2$ are mixed with states $\mp 3/2$, forming two states Γ_7. The three states denoted as Γ_6 originate from the mixing of the states $\pm 9/2$, $\pm 1/2$ and $\mp 7/2$. The magnetic moment associated with the Kramers-doublet states is opposite causing their exact cancellation and yielding local zero-moment [12]. The double Kramers degeneracy, associated with the time-reversal symmetry, can be removed only by external/internal magnetic fields. The splitting of the Kramers doublet means the appearance of the local moment as the exact cancellation of the two-states moment is no longer maintained. The unique feature of the Kramers systems relies on the fact that the Kramers degeneracy has to be removed before the absolute-zero temperature is reached. If spin-dependent interactions are weak then the system has difficulty in the removal of the Kramers degeneracy leading to small splitting of the Kramers doublet as small as a parts of kelwin. Then large
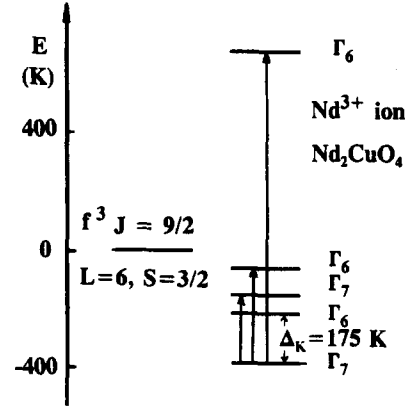

Fig. 2. The fine electronic structure, consisting of five Kramers doublets with internal splitting below 0.5 meV, of the Nd^{3+} ion in Nd_2CuO_4 as determined by inelastic-neutron-scattering experiments [4–8]. Arrows indicate excitations observed in INS experiments. This energy level scheme is fully accounted for by charge interactions of the aspherical $4f$ shell with the crystal field of the tetragonal symmetry – the shown eigenfunctions result from CEF parameters: $B_2^0 = +11.6$ K, $B_4^0 = +155$ mK, $B_6^0 = -0.5$ mK, $B_4^4 = -175$ mK and $B_6^4 = -34$ mK. The shown states are many-electron states. The population of these states is governed by the Boltzmann-distribution function – at the absolute zero temperature only the lowest state is occupied. With increasing temperature higher states become occupied.

specific heat can be observed at ultra-low temperatures [13]. From this respect Kramers systems like f^1 (Ce^{3+}), f^3 (Nd^{3+}, U^{3+}), f^5 (Sm^{3+}) or f^{13} (Yb^{3+} ion) are of great interest also owing to the fact that many of these compounds exhibits heavy-fermion behaviour.

3. DISCUSSION

The fine electronic structure of the Nd^{3+} ion in Nd_2CuO_4, resulting from the charge interactions, is shown in Fig. 2. Such the structure is derived by means of INS experiments [4–8]. There is good agreement between different experimental/theoretical research groups about the energetical positions of the bound states, at 15, 21, 27 and 95 meV as well as about their localized character. A discussion is still going on on the assignment of the eigenfunctions Γ_i to the states and consequently about the particular values for the CEF parameters. In discussion of implications of the existence of the FES it should be remembered that the discussed states are many-electron states of the whole f^3 system and that at the absolute-zero temperature only the ground state is populated. The overall splitting of the FES amounts in Nd_2CuO_4 to 0.1 eV which is four times more than in $NdNi_5$ [9–11]. It indicates that CEF interactions are a few times

stronger in ionic compounds than in intermetallics. The separation to the first excited state plays an important physical role. Many magnetic and electronic properties exhibit some distinct anomalies at temperatures compared with the energy separation to the first excited state Δ_K. The specific heat, for instance, exhibits a maximum at about $0.42\Delta_K$ provided other states are much higher. It is just the case of Nd_2CuO_4 where the first-excited doublet lies at 175 K. A Schottky-type peak associated with this doublet can be hardly detected by specific-heat experiments owing to the large phonon contribution at temperatures above 50 K. It is a reason why INS studies are so important in determination of localized states in rare-earth compounds.

However, specific-heat experiments are especially suited to study the low-energy part of the energy-level scheme. In particular, they are very useful in studies of the formation of the two closely-lying localized states. In the present case, the two closely-lying localized states appear after removal of the double Kramers degeneracy by spin-dependent interactions. The splitting of the Kramers doublet ground state in the Nd_2CuO_4 is small as the effective magnetic field acting on the Nd-ion moment is small. It is due to almost exact cancellation of the molecular field at the Nd site caused by the antiferromagnetic arrangement of the magnetic Cu ions. From a rough analysis of the specific heat of Nd_2CuO_4 with a pronounced maximum at 1.9 K, as shown in Fig. 3, one obtains an approximate value of the splitting δ_K of 4.5 K (0.4 meV). For more exact calculations the following Hamiltonian including CEF interactions and spin-dependent interactions has been considered:

$$H_R = \sum_{n=0}^{6}\sum_{m=0}^{n} B_n^m O_n^m$$

$$- g\mu_B \cdot (ng\mu_B J\langle J \rangle - 1/2ng\mu_B \langle J \rangle^2 - J \cdot B_{eff}). \quad (2)$$

The second term represents the Nd–Nd spin-dependent interactions, written in the mean-field approximation, where g (= 8/11) and J (= 9/2) are Lande factor and the total angular momentum of the Nd^{3+} ion, respectively. B_{eff} represents an effective molecular magnetic
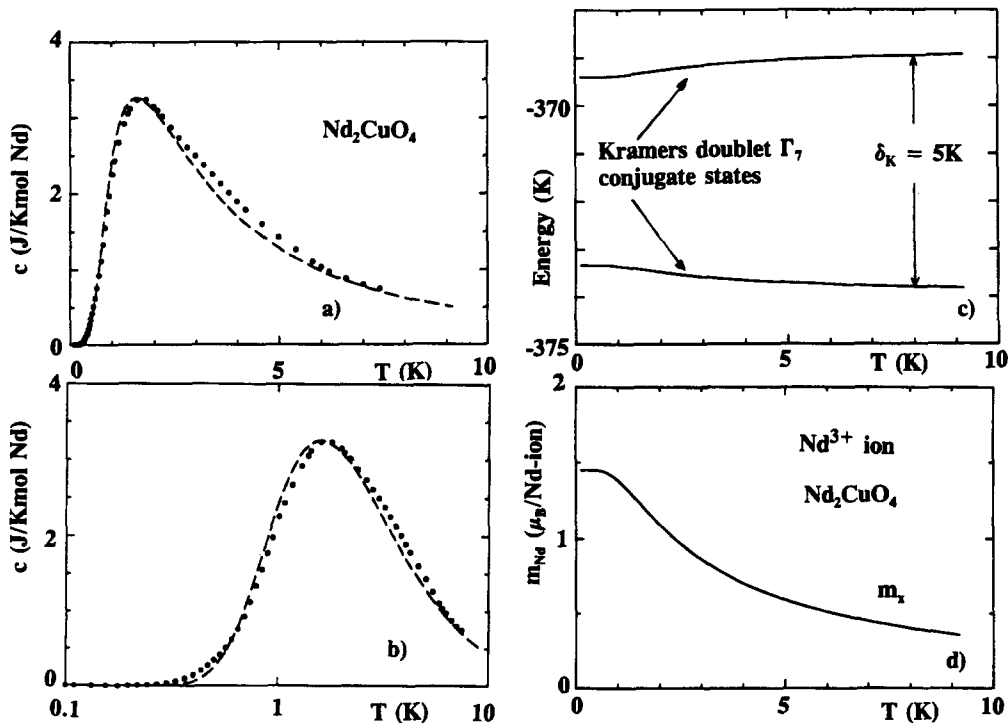

Fig. 3. The temperature dependence of the specific heat in Nd_2CuO_4 (a, b). Markers represent data taken after [1]. The dashed line is calculated assuming localized Nd^{3+} -ion excitations within the Kramers-doublet CF ground state. (c) The splitting δ_K of the Kramers doublet ground state Γ_7, as the function of temperature derived from the analysis of the temperature dependence of the specific heat. δ_K is very small, at 9 K it amounts to 5 K (0.4 meV) only. Its slight decrease with decreasing temperature is caused by the antiferromagnetic Nd–Nd spin interactions. This effect causes deviation of the c(T) dependence from the well known Schottky curve for the stable two-level system. (d) Calculated temperature dependence of the local Nd-ion magnetic moment, directed along the x direction, that is in good agreement with neutron-diffraction data [15].

field acting on the Nd-ion moment. It is largely generated by the (antiferromagnetic) Cu moments. As will be shown later the Nd–Nd interactions become visible at temperatures below 10 K.

Before the detailed analysis of the low-temperature specific heat a full set of 5 CEF parameters, relevant to the tetragonal symmetry, have been evaluated in order to reproduce the observed localized excitations. A found set of CEF parameters: $B_2^0 = +11.6\,K$, $B_4^0 = +155\,mK$, $B_6^0 = -0.5\,mK$, $B_4^4 = -1.75\,mK$ and $B_6^4 = -34\,mK$ reproduces the experimentally observed energy level scheme. The resulting scheme of 0–174–242–338–1101 K is in good accord with the observed one of 0–174–242–313–1102 K [8]. The present set of CEF parameters is somehow close to that given in [4]. But contrary to the set presented in [4] the present set gives the local Nd moment predominantly along the x direction, not along the z direction as wrongly yields the set presented in [4]. The x-preference of the Nd-ion moment has been experimentally found by neutron diffraction [14, 15]. The present set of CEF parameters yields Γ_7 as the charge-formed Kramers doublet ground state, Fig. 2. Until now in most of publications the state Γ_6 has been considered as the ground state. Apart from the good reproduction of the Nd-moment direction the present set of CEF parameters is in agreement with intensities of transitions observed in INS experiments, i.e. the two most intensive transitions are at 242 K and 337 K as is observed. Our set of CEF parameters with zero-temperature value for the magnetic moment of $1.40\,\mu_B$ for the Nd moment that lies in the tetragonal plane is strongly supported by neutron-diffraction studies of Matsuda et al. [14] who found a moment of $1.3\,\mu_B$ at 0.6 K. Moreover, the calculated temperature dependence of the Nd magnetic moment, shown in Fig. 3d, is in very good agreement with neutron-diffraction experiments [15] that yield a Nd moment of $0.44\,\mu_B$ at 4.1 K and a moment of $0.17\,\mu_B$ only at 12.3 K.

By the fitting of the temperature dependence of the specific heat $c(T)$ for the system Nd_2CuO_4 it has been found that $B_{eff} = 2.8\,T$ and $n = -0.5\,T/\mu_B$. The very good description, shown in Fig. 3a, b, in combination with reproduction of the INS results, confirms that the low-temperature specific heat observed in Nd_2CuO_4 is indeed caused by the localized f-electron excitations to the Kramers conjugate state over the energy gap δ_K. The good reproduction of the specific heat also indicates that the value of δ_K is almost the same at different Nd sites through the macroscopic sample involving $\sim 10^{22}$ Nd ions and that all Nd ions experience the same magnetic and electric fields. Such behaviour is a characteristic of a system with a good long-range magnetic order. This long-range magnetic order is set

up by Cu-ion moments – there is no spontaneous order of the Nd ions as is indicated by the rounded-shape of the low temperature specific heat. The Nd-ion moment is induced by the molecular field set up by the magnetic Cu ions. As has been pointed already the splitting of the Kramers doublet is equivalent to the existence of the local magnetic moment [12]. Its value rapidly decreases with temperature as the difference in population of both the Kramers conjugate states decreases. The splitting of the Kramers-doublet ground state, shown in Fig. 3c, exists above 10 K diminishing eventually at $T_N = 260\,K$.

By Ce substitutions, the localized f-electron excitations are shifted to lower temperatures as the gap δ_K decreases. The decrease of δ_K is caused by the decrease of Cu–Cu magnetic interactions inferring from the experimentally observed decrease of the Neél temperature. In substituted systems the distribution of δ_K can exist, i.e. δ_K becomes site-dependent, in particular when a complex magnetic structure is formed. It is worthwhile to add that Ce^{3+} ions, if present, having the Kramers doublet ground state, will also contribute to low-energy excitations. All these effects will lead to the broadening of the peak, the deviation from the well-known Schottky curve and the shifting of the localized excitations to lower temperatures in Ce-doped Nd_2CuO_4 compounds. This trend is in agreement with the observation shown in Fig. 1. The careful analysis of the specific heat for the sample $y = 0.1$, i.e. for the sample $(Nd_{0.95}Ce_{0.05})_2CuO_4$ has revealed the existence of two localized contributions with gaps δ_K of 3.2 K and δ_K' of 1.0 K, see Fig. 4. and with the ratio of the involved entropy close to 0.95/0.05. It would indicate that the gap δ_K corresponds to the Nd-ions whereas the δ_K' originates from the Ce ions. Another possibility, that it originates from some Nd ions that found themselves in a much smaller internal field is rather improbable as then one would expect the ratio between two peaks to be more balanced, i.e. 1 : 1, 1 : 2 or 1 : 3 and so on. Thus, surprisingly, this analysis indicates that some of the Ce ions are in the trivalent state. The internal field B_{eff} is almost the same (2.7 T) and n slightly increases $(-0.7\,T/\mu_B)$. In general, we note that the increase of the AF Nd–Nd interactions causes the lowering of the maximum of the Schottky-type peak and its more rounded shape. This rounded shape is more visible in Fig. 4b for the sample $Nd_{1.85}Ce_{0.15}CuO_4$. Values $B_{eff} = 3.2\,T$ and $n = -1.5\,T/\mu_B$ have been used for the calculations. The increase of n with the Ce doping, however, could indicate the increase of conduction-electron density pointing to the tetravalency of the Ce-doped ions. Two distinct Schottky-type anomalies at
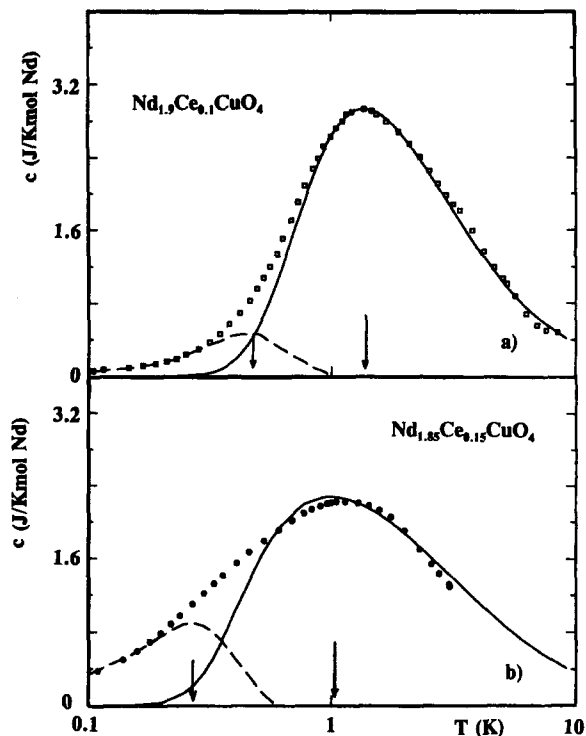
Fig. 4.(a) The analysis of the specific heat for $Nd_{1.9}Ce_{0.1}CuO_4$ revealing the existence of two energy gaps δ_K (= 3.2 K) and δ'_K (= 1.0 K) with the involved entropy with the ratio of 0.95/0.05. They are atributed to the Nd^{3+} and Ce^{3+} ions, respectively. The solid line represents the specific heat calculated with $B_{eff} = 2.7$ T and $n = -0.7$ T/μ_B. Points are experimental data taken after [1]. The dashed line represents the difference between the experimental data and the calculated Nd contribution. (b) The analysis of the specific heat for the sample $Nd_{1.85}Ce_{0.15}CuO_4$ revealing the existence of two energy gaps δ_K (= 2.5 K) and δ'_K (= 0.6 K). For calculations value $B_{eff} = 2.7$ T and $n = -1.5$ T/μ_B have been used.

temperatures 1.0 K and 0.25 K are observed. They indicate the existence of two energy gaps with δ_K of 2.4 K and 0.6 K. It is necessary to mention that the lower peak is quite substantial. As it is ultra-low temperature range we suppose that part of this peak is built up from Nd-nuclear excitations.

It is worth pointing out that despite the detailed shape of the specific heat the theoretical entropy involved in the low-temperature specific heat will always amount to $R\ln 2$ as it is associated with excitations within two closely-lying localized states. The total entropy for four $Nd_{2-y}Ce_yO_4$ compounds, calculated up to 10 K on the experimental data of [1], amounts to $R\ln 2$, within experimental error, confirming the existence of a two (localized) states. In our calculations this entropy amounts to $R\ln 2$. The

entropy, associated with the excited CEF level(s) is not visible at a temperature of 10 K.

4. CONCLUSIONS

The large ultra-low temperature heat observed for the Nd_2CuO_4 samples has been quantitatively explained as caused by the localized many-electron low-energy excitations of the highly-correlated f^3 electronic subsystem of the Nd^{3+} ions. The localized excitations are associated with the removal of the Kramers degeneracy of the Kramers doublet charge-formed ground state due to inexact cancellation of the molecular field at the Nd sites set up by the magnetic Cu ions. Two closely-lying localized states are formed with a small energy separation δ_K. From analysis of the temperature dependence of the specific heat of Nd_2CuO_4, with a rounded maximum at 1.9 K, δ_K of 0.55 meV at 9 K has been found. Moreover this small gap δ_K slightly decreases with lowering temperature indicating antiferromagnetic Nd-Nd interactions. With the Ce substitutions δ_K decreases much more quickly and becomes site-dependent resulting in the shifting of the localized excitations and consequently specific heat to lower temperatures. The present explanation within the localized f-electron picture is supported by the inelastic-neutron-scattering results [8, 15] which have revealed that the multiplet structure is preserved in the Ce-doped compounds though they exhibit superconductivity.

Similar large low-temperature specific heat due to the removal of the Kramers degeneracy of the localized f electrons has been discussed in intermetallic compounds like $NdNi_5$ or $ErNi_5$ both from experimental as well as the theoretical point of view [8, 9, 11]. Studies of systems containing Kramers paramagnetic ions is of great interest as the removal of the Kramers degeneracy, with δ_K even of parts of kelwin, have been proposed to be the origin of the heavy-fermion phenomena [10, 13, 16].

One should not be surprised by different sets of CEF parameters given by different groups. It only reflects difficulties in finding the unique description of charge interactions but there is no doubt about the localized nature and the CEF origin of the discussed excitations in $Nd_{2-y}Ce_yCuO_4$ compounds. There is, however, a need for experimental results giving information about the eigenfunctions. From this respect the full agreement with neutron-diffraction data about the value and the direction of the Nd-ion moment provides a strong argument in favour of the present set of the CEF parameters.

in computer analysis of specific heat data is highly appreciated.

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