Spin-glass freezing above the ordering temperature for the Kondo ferromagnet $CeNi_{0.4}Cu_{0.6}$

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The low-temperature magnetic and transport properties of the orthorhombic $CeNi_{0.4}Cu_{0.6}$ compound have been determined from the analysis of specific heat, ac magnetic susceptibility, electrical resistivity, elastic and inelastic neutron scattering. These measurements present intriguing experimental results that could not be explained within the usual phenomenology of Ce-based compounds. C_p and χ_{ac} present anomalies around 1 K corresponding to ferromagnetic order as confirmed by neutron diffraction. The magnetic structure is collinear with very reduced moments, 0.6 μ_B/Ce lying in the b direction. Additionally, a clear Kondo behavior is observed with a Kondo temperature $T_K = 1.9$ K estimated from quasielastic neutron scattering. Above the ordering temperature, further anomalies are observed in C_p and χ_{ac} that could not be explained as originating from crystal electric field or Kondo effects. From the frequency and field dependence of the χ_{ac}, above T_c, a spin-glass state with a freezing temperature $T_f = 2$ K is proposed for this compound. This unusual magnetic behavior is discussed in terms of mixed (positive and negative) Ruderman-Kittel-Kasuya-Yosida interactions, randomness (structural disorder), large hybridization (Kondo effect), and strong magnetocrystalline anisotropy (crystal electric field effects). [S0163-1829(97)05242-9]

I. INTRODUCTION

Among the different issues of the strongly correlated electrons systems, the study of heavy fermions close to the magnetic instability and the non-Fermi-liquid (NFL) state merits special attention. In particular, the NFL behavior, observed on a number of intermetallic Ce- and U-based compounds, appears as an intriguing phenomena and several approaches, both theoretical and experimental, have been developed.[1,2] In this way, different microscopic origins have been invoked, as quadrupolar Kondo interactions and collective magnetic fluctuations effects for the $U_xY_{1-x}Pd_3$,[3,4] $U_{0.9}Th_{0.1}Be_{13}$,[5] or Ce_7Ni_3,[6] and especially the incipient antiferromagnetic order on $CeCu_{5.9}Au_{0.1}$.[7] In the latter system, it is clear that the nature of the ground state depends on the delicate balance between the on-site Kondo interaction, which favors a local nonmagnetic singlet, and the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interactions, which via the conduction electrons, tend to establish long-range magnetic order.

The understanding of such competition is the key to a deeper analysis of these systems and for a long time the Doniach diagram[8] provided a useful qualitative description. According to this framework, the evolution of the magnetic properties of anomalous Ce, Yb, or U compounds have been studied with real[9] or chemical pressure.[10] Continuous theoretical improvements have been done, incorporating strong local exchange[11] and short-range magnetic correlations above the critical temperature.[12] Most of the referred examples develop antiferromagnetic order, but there exist other situations where ferromagnetic order appears, as is the case of $CeNi_{1-x}Pt_x$ compounds.[13] In this system, a direct relationship between the increasing $4f$ conduction-band hybridization (Kondo interaction) and the decreasing cell volume has been found when we move from CePt to CeNi, explaining the magnetic instability (magnetic→nonmagnetic transition) which appears around $x = 0.1$.[14]

On the other hand, the magnetic properties of RNi$_{1-x}$Cu$_x$ compounds (R = Nd or heavy rare earth) show a transition from ferromagnetism in RNi to antiferromagnetism in RCu.[15,16,17] Although CeNi crystallizes in the orthorhombic CrB-type structure, the FeB phase of CeCu is stabilized for $x \geqslant 0.2$. Both crystallographic structures only differ in the spatial arrangements of rare-earth trigonal prisms with a transition-metal ion in the center[18] and Ce-(Ni,Cu) and Ce-Ce nearest-neighbors distances increase slightly with the Cu concentration; the corresponding cell volume increase is comparable to those of the $CeNi_{1-x}Pt_x$ system.[19] Two effects are expected in $CeNi_{1-x}Cu_x$ series when Ni is substituted by Cu: on the one hand, a decrease of the hybridization associated with the increase of the cell volume, which leads to a change from nonmagnetic to localized Ce magnetism; and, on the other hand, a change from ferromagnetism for compounds with large Ni content to antiferromagnetism for CeCu ($T_N = 3.6$ K), which is associated with modifications in the competing ferro-antiferro interactions mainly induced by the changes in the density of states at the Fermi level.[20]

A preliminary magnetic characterization of $CeNi_{1-x}Cu_x$ compounds was recently presented.[19] The crossover from delocalized to localized behavior seems to be close to $x \approx 0.2$, and clear indications of the coexistence of ferromagnetism and Kondo interactions were found for $0.2 < x \leqslant 0.8$, while CeCu and $CeNi_{0.1}Cu_{0.9}$ behave as antiferromagnets with very small traces of Kondo interactions. This situation is especially attractive because in these compounds the Kondo interaction appears to be more intense for the ferromagnetic compounds than for the antiferromagnetic ones.

In particular the $CeNi_{0.4}Cu_{0.6}$ compound appears as a good candidate to study the interplay between competing ferro-antiferromagnetic RKKY interactions and Kondo effect in a local low-symmetry system. A first analysis of resistivity and magnetization down to 2 K (Ref. 21) suggests a ferromagnetic ordering with T_c below 2 K and shows clear indications of a Kondo behavior with T_K larger than T_c.

In this paper, we report electrical resistivity, ac magnetic susceptibility, specific heat, and neutron-scattering measurements performed in $CeNi_{0.4}Cu_{0.6}$ at very low temperatures down to mK range.

II. EXPERIMENTAL DETAILS

The polycrystalline sample has been obtained in an arc furnace under Argon atmosphere and annealed for six days at 425 °C under high vacuum. The quality of the sample and the absence of spurious crystallographic phases have been checked by x-ray and neutron diffraction. The homogeneity of the sample was also tested by x-ray dispersive analysis. The electrical resistivity, ac susceptibility ($\nu = 159$ Hz, $h_{ac} = 10$ mOe) and specific heat were measured in the temperature range 300 mK–5 K at the laboratories of the I.C.M.A. (Zaragoza, Spain). A ^{3}He-^{4}He dilution refrigerator was used for the ρ and χ_{ac} measurements. For each point the temperature was regulated to within ≈ 1 mK. The heat capacity was measured in a quasiadiabatic calorimeter cooled by adiabatic demagnetization process. The points were obtained by the heat-pulse technique. The relative error is less than a few percent.

Electrical resistivity above 2 K and the dependences with frequency and applied magnetic field of the ac susceptibility above 1.9 K were measured in the laboratories of the Universidad de Cantabria (Santander, Spain). Neutron-diffraction experiments were carried out on the D1B diffractometer equipped with dilution cryostat, down to 100 mK and inelastic neutron scattering above 1.5 K was performed in IN6, time-of-flight spectrometer, both instruments installed at the Institut Laue Langevin (Grenoble, France).

III. RESULTS AND ANALYSIS

A. Specific heat

In Fig. 1, the low-temperature specific heat, after subtracting the phonon contribution (C_p-$C_{p\,\mathrm{phon}}$) of $CeNi_{0.4}Cu_{0.6}$ down to 300 mK, is presented. In the investigated temperature range, we have considered as phonon part, after taking into account the mass correction, a Debye law corresponding to the nonmagnetic isomorphous (FeB-type structure) YNi compound ($\theta_D = 228$ K).[22] In any case, for the very low-

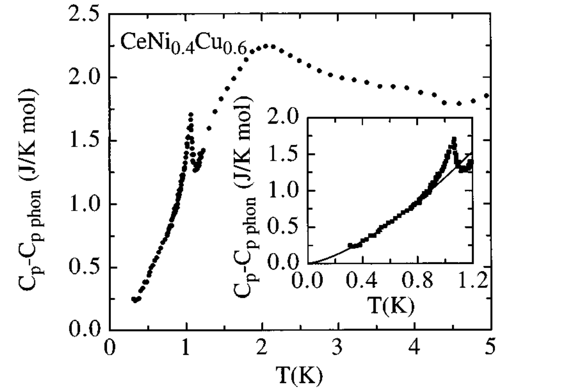

FIG. 1. Temperature dependence of the specific heat after subtracting the phonon contribution. Inset shows the low-temperature contribution fitted to a $\gamma T + \beta T^{3/2}$ law in the range $0.3\,\mathrm{K} < T < 0.9$ K.

temperature range considered in this study, the phonon term is almost negligible. From this figure a clear λ-like anomaly at 1.1 ± 0.1 K and a broad hump centered about 2.0 ± 0.1 K are observed. The λ-like anomaly corresponds to the Curie temperature, as it will be later corroborated by neutron-diffraction experiment (see Sec. III D). The origin of the huge anomaly appearing above T_c is not obvious at this step and will be deeply analyzed later on in the text.

The electronic coefficient of the specific heat γ could give valuable information about the Kondo interaction. However, in the present study, its determination is a difficult task, because of the small range of temperature measured, and the hump anomaly at 2 K that is superimposed to the expected linearity above T_c. Considering the whole temperature range studied we could estimate from the extrapolation to 0 K of the linear behavior of C_p-$C_{p\,\mathrm{phon}}/T$ vs T^2 for $T \gg T_c$ a rough high limit for γ of about 350 mJ/K^2 mol; let us underline that due to the extra contributions existing above T_c this extrapolation gives us only an order of magnitude of the γ value. Additionally for $T < T_c$ in a three-dimensional ferromagnet, as it is the case for $CeNi_{0.4}Cu_{0.6}$, a C_p-$C_{p\,\mathrm{phon}} = \gamma T + \beta T^{3/2}$ law is expected. Such fit provides a γ value of 100 mJ/K^2 mol (see inset of Fig. 1). The introduction of an $\exp(-\Delta/T)$ term (strong anisotropic ferromagnet)[10] leads to considerable higher γ values, up to 600–700 mJ/K^2 mol. In spite of the different estimations of γ, its enhanced value indicates the heavy fermion character of this compound.

The importance of the large reduction of the λ anomaly magnitude ΔC_{mag} at T_c (0.6 J/K mol) with regard to the expected value 12.48 J/K mol corresponding to a crystal electric field (CEF) doublet ground state should be evaluated analyzing the Kondo effect. A correlation between this reduction and the ratio T_K/T_c of the Kondo to the Curie temperature has been established within the $S = \frac{1}{2}$ resonant-level model using a mean-field approach.[23] The explicit relation for the specific-heat jump ΔC_{mag} at T_c is given by[14]

$$\Delta C_{mag} = \frac{6K_B}{\psi'''(\frac{1}{2}+\xi)}\,[\psi'(\tfrac{1}{2}+\xi\psi''(1+\xi))]^2, \qquad (1)$$

where $\xi = 1/2\pi\; T_K/T_c$ and Ψ', Ψ'', and Ψ''' are the first three derivatives of the digamma function. This analytical

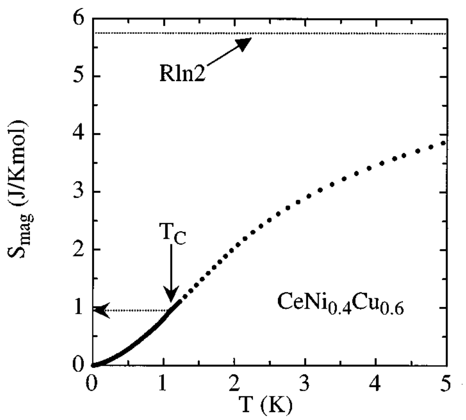

FIG. 2. Temperature variation of entropy after subtracting the phonon contribution, the arrow indicates the ordering temperature T_c. Note that even at 5 K the entropy is still far from the R ln2 value corresponding to a doublet ground state.

variation gives a value of $T_K = 5.77$ K for the observed ΔC_{mag}. Furthermore, the magnetic entropy at $T_c = 1.1$ K (see Fig. 2) is about 0.91 J/K mol, which is far from the value 5.76 J/K mol corresponding to R ln2 of the filling up of the doublet ground state. Moreover, from the magnetic entropy, we can also obtain an estimation of T_K using a simple two level model with an energy splitting of $k_B T_K$:[24]

$$\frac{\Delta S}{R} = \ln[1+\exp[(-T_k)/T_c]] + \frac{T_k}{T_c}\frac{\exp[(-T_k)/T_c]}{1+\exp[(-T_k)/T_c]}. \tag{2}$$

The T_K obtained from this method is 4.2 K, quite close to that previously determined from the ΔC_{mag}.

Finally, in order to account for the hump centered about 2.0 K different models have been considered. In particular, the Kondo resonance and CEF effects could give, *a priori*, valuable contributions below and above T_c. In fact, the Ce ($J = \frac{5}{2}$) ions lie, in this orthorhombic FeB structure, on a very low-symmetry site and the CEF effects are important, leading to three doublets that are split by the Kondo interaction. The CEF level scheme in other orthorhombic similar compounds as CePt (Ref. 25) gives a total splitting larger than 200 K with a first excited doublet lying at $\Delta_1 \approx 140$ K. Moreover, inelastic neutron scattering (INS) results on $CeNi_{0.4}Cu_{0.6}$ (see Sec. III E) do not show any trace of CEF transitions below 2 meV. For all of these reasons we can consider CEF effects irrelevant below 5 K. Then, the important hump centered around 2 K should reflect, in principle, the contribution corresponding to the Kondo ''splitting'' of the first CEF doublet. This possibility seems to be supported by the magnetic entropy analysis presented in Fig. 2; as it has already been commented, at $T_c = 1.1$ K the entropy value is 0.91 J/K mol, and then it increases with increasing T, approaching the R ln2 value, which corresponds to the thermal population of the low-lying CEF ground-state doublet. The calculation of a single Schottky-like term, with a splitting corresponding to $T_K = 5$ K is reported in Fig. 3. Although with this splitting the position of the maximum at 2 K is well accounted for, the calculated contribution is much larger ($\approx 50\%$) than the measured one.

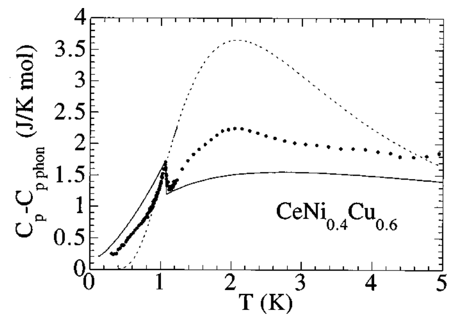

FIG. 3. Specific heat as a function of temperature. The full line represents a fit to the resonance level model (Ref. 23) and the dotted line corresponds to a Schottky contribution from the lifting of degeneracy by 5 K of the doublet ground state due to Kondo effect (see text).

Another possibility is to compare the whole profile of C_p-$C_{p\ phon}$ between 300 mK and 5 K, with calculations performed considering the long-range magnetic order and the Kondo effect on the low-lying doublet level in the scope of the previously mentioned mean-field theory.[23] However, in these calculations the only two parameters to be varied, the exchange energy J and T_K, are fixed from the experimental data T_c and ΔC_{mag} (from $T_c = 1.1$ K and $\Delta C_{mag} = 0.6$ we get $J = 9.9$ K and $T_K = 5.77$ K). The comparison between experimental and calculated data is also reported in Fig. 3. Although a maximum appears at similar temperatures (about 2 K) for both sets of data, marked differences are obtained. In particular, the curve shape is not similar and an extra entropy contribution should be needed to account for the notorious experimental hump observed. More general calculations of the overall shape of C_p with freedom in the J and T_K do not improve the fitting results.

B. ac susceptibility measurements

The real and imaginary part of the magnetic susceptibility χ' and χ'' are depicted in Fig. 4. Both anomalies, reported previously in C_p, are again detected, i.e., a quite marked peak in the paramagnetic phase around 2 K and a shoulder at 1 K corresponding to the Curie temperature. The fact that both features are also observed in the imaginary part of the magnetic susceptibility χ'' provides new important consequences. Although the ferromagnetic transition at $T_c = 1.1$ K (λ-like anomaly in C_p) has a second order character, the shoulder observed in χ'' at 1.1 K corresponds to the motion of narrow domain walls that appear in strong anisotropic ferromagnetic compounds. The susceptibility is almost zero at low temperatures, and starts to increase at temperatures at which the thermal activation and/or the applied magnetic field are large enough to produce the domain-wall motion overcoming the anisotropy responsible for the quenching of these magnetic domains. This narrow wall behavior has already been observed in the ferromagnetic $NdNi_{1-x}Cu_x$ compounds,[17] which have the same crystalline structure. A guide for the eyes of such behavior together with the contribution of the anomaly at 2 K is presented in Fig. 4 as dashed lines.

Concerning the peak observed around 2 K, which must be related to the hump anomaly observed in C_p at a similar

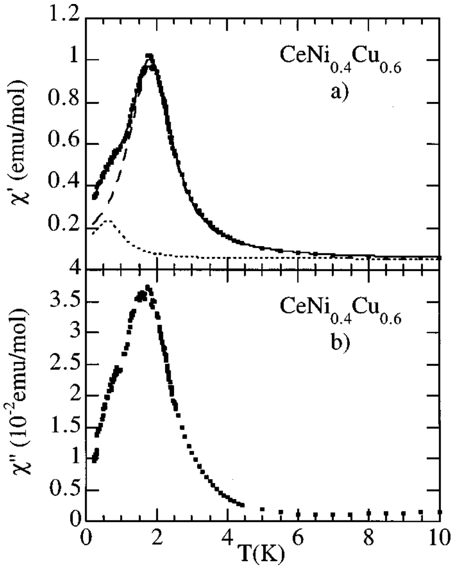

FIG. 4. Real and imaginary part of the ac magnetic susceptibility vs temperature in zero applied magnetic field. Dashed lines indicate the two contributions to the susceptibility as explained in the text. The experimental data coincides with the sum of both.

temperature, these susceptibility measurements evidence that some kind of irreversibility is associated with this experimental feature since it also appears in χ''. A calculation considering Kondo effect in the Bethe-Ansatz solution for $S=\frac{1}{2}$ of the Coqblin-Schrieffer model[26] leads to a very smoothed anomaly, in contrast to the well marked peak observed.

In order to get a deeper understanding of the nature of the 2 K peak we have performed frequency and field dependence χ_{ac} measurements that are presented in Fig. 5. The maximum of the real part of the susceptibility [Fig. 5(a)] shifts to

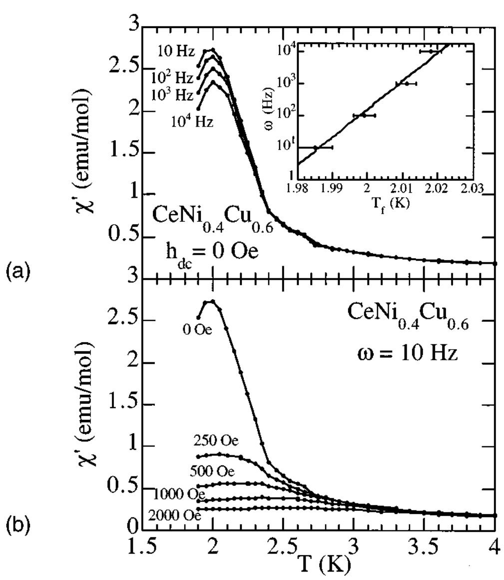

FIG. 5. (a) Temperature variation of the real part of the ac susceptibility measured at different frequencies. The inset shows a fit of the position of the susceptibility maximum to a Vogel-Fulcher law. (b) Temperature dependence at 10 Hz of the real part of the ac susceptibility under different applied magnetic fields.

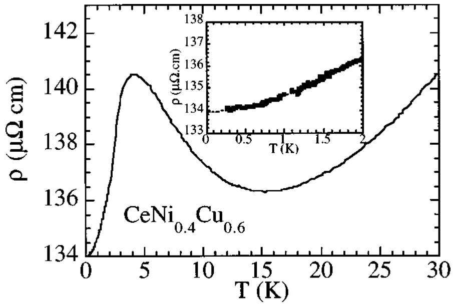

FIG. 6. Temperature dependence of the electrical resistivity. Inset shows the $T<2$ K variation fitted to a $\rho=\rho_0+AT^2$ law.

higher temperatures ($\approx 2\%$) and its value slightly decreases with increasing frequency. An applied magnetic field [Fig. 5(b)] of 250 Oe reduces the magnitude of the χ' peak to 25% while a 2000 Oe magnetic field completely cancels the observed anomaly. Accordingly, the maximum of χ'' follows the same field dependence.

C. Electrical resistivity

The low-temperature electrical resistivity ρ of $CeNi_{0.4}CU_{0.6}$ between 300 mK and 3 K perfectly overlaps with the measurements previously reported[21] (see Fig. 6) and does not show any anomaly around $T_c=1.1$ K, as observed in the inset of Fig. 6. It is worthwhile to remember that in the magnetic entropy variation (Fig. 2) no marked anomaly was detected at T_c. This fact is certainly due to the low magnetic contributions, suggesting that the magnetic Ce moments are quite reduced in this system. The extrapolation below 300 mK leads to a residual resistivity value of 133.9 $\mu\Omega$ cm. Fitting to a $\rho=\rho_0+AT^2$ law at low temperatures (solid line in the inset of Fig. 6) and using the $A/\gamma^2=10^{-5}$ $\mu\Omega$ cm mJ^{-2} K^2 mol^2 relation, usually found in heavy fermions,[27] a γ value of 250 mJ/K^2 mol is estimated. The wide minimum observed in the high-temperature range about 14 K followed by a clearly marked maximum ρ_{max} centered around 3.8 K are frequently found in Kondo systems. But in our case, the position of the maximum does not correspond to T_c as it usually occurs in Kondo compounds when $T_c>T_K$. In fact, this resistivity is clearly reminiscent of a Kondo concentrated compound with a coherence temperature corresponding to the resistivity maximum ρ_{max}.

D. Magnetic structure

As commented in the Introduction, the shape of the magnetization curves down to 2 K (Ref. 21) suggest a long-range ferromagnetic order at lower temperatures. This behavior is confirmed by the low-temperature neutron-diffraction study. In Fig. 7 we present the magnetic diffraction pattern obtained by subtraction of the two diagrams at 100 mK and 5 K. Only the nuclear reflections show extra magnetic intensity and the Rietveld analysis leads to collinear ferromagnetic order along the b direction with magnetic moments of 0.6 μ_B/Ce, which is a strongly reduced value with respect to that of the Ce^{3+} free ion (2.14 μ_B/Ce). The neutron pattern at 2 K does not show any trace of magnetic intensities. These neutron-diffraction results are conclusive with respect to the nature of

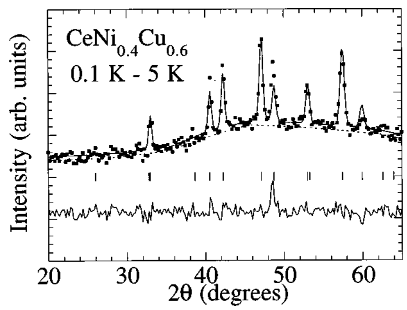

FIG. 7. Magnetic neutron-diffraction pattern (difference between 0.1 and 5 K). Points indicate the experimental data, lines are the calculated and difference patterns. Vertical ticks mark the magnetic reflections. The background hump is due to the incoherent scattering of ^{3}He used in the dilution cryostat.

the ferromagnetic order and the T_c value, as well as the strongly reduced value of the Ce magnetic moment, which is a sign of the importance of Kondo effect.

It is also worthwhile to mention that, in these pseudobinary orthorhombic compounds, the b direction seems to be favored as the ferromagnetic one by the exchange interactions at low temperatures, i.e., $GdNi_{1-x}Cu_x$ (Ref. 16) or $Ho_{1-x}Y_xNi$,[28] while the CEF tends to maintain the moments in the (a,c) plane. Then, it is not surprising that a ferromagnetic Fy component appears at low temperatures in this compound.

E. Inelastic neutron scattering (INS) experiments

The INS spectrum obtained for $E_0=3.1$ meV incoming neutrons at 1.7 K and $Q=0.42$ Å^{-1} is represented in Fig. 8. A first view of the spectrum clearly shows a quasielastic contribution. It is quite important to mention a peculiarity of this quasielastic spectrum at 1.7 K. This spectrum cannot be fitted with a single Lorentzian curve shape. It is necessary to include a Gaussian contribution centered at 0.45 meV to account for the experimentally observed intensity.

The Lorentzian quasielastic half width $\Gamma/2$ is given as function of temperature in the inset of Fig. 8. The dependence of $\Gamma/2$ shows a rather linear behavior up to 60 K. This temperature dependence (Korringa law) usually appears for magnetically ordered Kondo systems.[29] From the extrapolation of $\Gamma/2$ to 0 K we extract a Kondo temperature of $T_K \approx 1.9$ K. The difference between the T_K values found from different methods (neutrons or bulk properties) has also been observed in other Ce systems and may reflect the different time scales of the experimental techniques. The most direct estimate is, of course, the quainelastic neutron scattering (QENS) value and then $T_K=1.9$ K must be considered as the more reliable value.

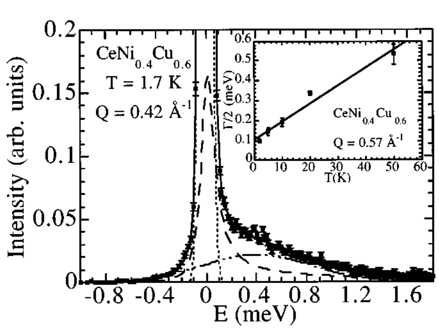

FIG. 8. Inelastic neutron-scattering spectra at 1.7 K. Full line represents a fit to the three contributions: elastic Gaussian (dotted line), quasielastic Lorentzian (dashed line), and inelastic Gaussian (dashed and dotted line). Inset shows the temperature dependence of the quasielastic Lorentzian linewidth for $Q=0.57$ Å^{-1}.

The above-mentioned contribution centered at 0.45 meV shifts to lower energies and decreases in intensity with increasing temperature, disappearing for $T \geqslant 10$ K. Furthermore, its half width increases as the temperature rises. For the **Q** range analyzed $(0.4<\mathbf{Q}<1.2$ Å$^{-1})$ this Gaussian contribution is almost **Q** independent. This excitation could not be attributed to a CEF transition; a similar anomaly has been detected in $YbAuCu_4$,[30] which orders below 1 K, and was interpreted by those authors as a precursor of the magnetic order.

IV. DISCUSSION

Summarizing, the low-temperature magnetic properties of $CeNi_{0.4}Cu_{0.6}$, in addition to the statement of ferromagnetic ordering below 1.1 K in this system, reflect several evidences of a marked Kondo character with an unusual magnetic behavior above T_c. The most notable features indicating Kondo effects are (i) the strong reduction of the Ce^{3+} magnetic moments obtained from neutron diffraction $\mu_{Ce}=0.6\,\mu_B$; (ii) the negative value of the paramagnetic Curie temperature $\theta_p=-10$ K obtained previously from the Curie-Weiss law at high temperatures,[21] from which a Kondo temperature $T_K=|\theta_p|/2=5$ K could be estimated; (iii) the analysis of the magnetic entropy (see Fig. 2), very reduced at $T_c=1.1$ K, which permits to estimate $T_K=4.2$ K; (iv) the QENS contribution leading to a $T_K=1.9$ K; (v) the minimum in the electrical resistivity at 13.5 K; (vi) the high estimated values of the γ coefficient. Thus, the coexistence of ferromagnetic order below $T_c=1.1$ K and Kondo interactions is well established from the present analysis.

However, some intriguing experimental facts need a further analysis. In particular, the behavior for $T>T_c$ with the anomalies observed around 2 K in C_p and χ_{ac} measurements. As presented and discussed in Secs. III A and III B, all attempts of accounting for our experimental results in C_p and χ_{ac} have not been satisfactory enough. In fact, a similar C_p hump was found in the $CeNi_2Sn_2$ heavy fermion compound,[31] and the authors estimate only 50% of the calculated Schottky anomaly to account for their experimental data, as could be also done in our present case. The reasons invoked by those authors for such reduction, i.e., broadening of CEF (acting at much higher temperatures in our case) or the reduction of magnetic entropy by Kondo effect (calculated in the fitting presented in Sec. III A), are not consistent in our case and we must question this 50% scaling procedure.

From these analyses we could confirm that the usual models of combining Kondo, CEF, and RKKY interactions only account partially for the anomalous behavior above T_c. Then a supplementary contribution is needed.

Considering the shape of χ', χ'' and the existence of the additional hump in the specific heat, the most plausible hypothesis is a freezing of the magnetic moments just above T_c, being $T_f \approx 2$ K the freezing temperature. The qualitative agreement with the usual spin-glass behavior[32] in χ_{ac}, C_P, and ρ is well accounted for in our compound, namely, (i) strong decrease of χ' below T_f, and the existence of a χ'' term about one order of magnitude smaller; (ii) the frequency and field dependence of χ_{ac} (Fig. 5): the maximum at 2 K shifts to higher temperatures as frequency increases ($\approx 2\%$, a typical value for spin-glass systems), and decreases strongly with low applied magnetic field, disappearing for $H \geqslant 2$ kOe; (iii) an additional contribution to the specific heat accounting for the entropy associated with the spin-glass state; (iv) the electrical resistivity increases with decreasing temperature, showing a maximum at temperatures above T_f, while no marked anomaly is observed in the vicinity of T_f.

From χ' frequency dependence [Fig. 5(a)], we could estimate the $\Delta T_f/[T_f \Delta(\log \omega)]$ value, T_f being the freezing temperature (maximum of the χ'). This value is 0.006, a characteristic one of spin-glass behavior.[33] Furthermore, following Mydosh analysis,[32] the frequency dependence of the maximum agrees with the empirical Vogel-Fulcher law [see inset of Fig. 5(a)]

$$\omega = \omega_0 e^{-E_a/T_f - T_0}. \quad (3)$$

The three fitted parameters $\omega_0 = 5.10^9$ Hz, $E_a = 0.7$ K, and $T_0 = 1.97$ K give consistent values with spin-glass behavior, considering that in our compound, T_f is about 2 K at 10 Hz. However, the absence of deeper theories for concentrated spin glasses prevents us from a further quantitative analysis.

The existence of spin glass or frustration effects has been quite frequently invoked in Ce- or U-based compounds to explain some intriguing experimental results; e.g., in the previously mentioned work on $CeNi_2Sn_2$ (Ref. 31) the authors claim for frustration effects but, as commented above, C_p measurements are not properly accounted for. On the other hand, $Ce(Cu_xGa_{1-x})_2$ compounds have also been a subject of controversy: spin glass[34] or antiferromagnetic state[35] was successively argued. For $CePd_{0.9}Ag_{0.1}$ (Ref. 36) the spin-glass behavior was found on samples obtained by rapid quenching and, recently, spin freezing in the Kondo CePtSn antiferromagnet was pointed out by muon spin rotation/relaxation techniques.[37] Finally, among the uranium alloys, URh_2Ge_2 (Ref. 38) has also been classified as a three-dimensional, random bond, heavy fermion spin glass; UPd_2Ge_2 presents a mixed spin-glass-ordered state at low temperatures,[39] and in diluted $U_xY_{1-x}Pd_3$ (Ref. 40) spin-glass behavior was also detected for certain U concentration ranges.

In most of these mentioned compounds, only one anomaly is found and the problem is to determine whether it corresponds to a spin-glass behavior or to a strong anisotropic antiferromagnetic state. In our case, we have a different situation because the ferromagnetic state of $CeNi_{0.4}Cu_{0.6}$ below 1.1 K, as well as the Kondo effect, are properly established. The questions are: How can the magnetic moments freeze above T_c and, are the conditions for the formation of a spin-glass state accomplished in our compounds?

Two are the well-known conditions for a ''cooperative freezing of spins'' without long-range spatial magnetic order: mixed (positive and negative) interactions and randomness (structural disorder). The first condition is easily fulfilled in our compound, as commented in the Introduction, since the change from ferro- to antiferromagnetism in the $RNi_{1-x}Cu_x$ (R = rare earth) series is observed for increasing Cu content. Although at low temperatures the ferromagnetic interactions are preponderant for $CeNi_{0.4}Cu_{0.6}$, the system is not far from the crossover to an antiferromagnetic order ($x \approx 0.85$). The competing interactions are an ''identity mark'' of these systems. The randomness is needed for the frustration of the long-range magnetic order; in our case, the disorder arises from the Ni/Cu crystallographic sites. Indeed, these ions provide different number of electrons to the conduction band, then it is expected that this influences locally the polarization of the conduction band, leading to an additional disorder on the magnetic interactions that arise not from a disorder on the magnetic sites but from the different contribution of each magnetic interaction acting on the Ce ions.

The complex phase diagram of this compound with successively Kondo ferromagnetism, spin freezing and paramagnetism, could be understood as due to the competing effects: mixed (positive and negative RKKY) indirect exchange interactions, large hybridization (Kondo interaction), and strong anisotropy (CEF). Such behavior could be qualitatively described as follows: at very low temperatures, the Kondo screening lowers the magnetic moment value reducing the Curie temperature with respect to that corresponding to a ''normal'' rare-earth [in the isostructural $NdNi_{1-x}Cu_x$ (Ref. 17) or $PrNi_{1-x}Cu_x$ (Ref. 41) compounds, the ordering temperatures are 20 times larger]. The magnetic interactions, although considerably weakened by Kondo effects, are strong enough to induce long-range magnetic order. For this particular composition $x = 0.6$, the order is ferromagnetic because positive interactions are still preponderant, as occurs for all the $RNi_{1-x}Cu_x$ (Refs. 15–17) compounds close to the RNi limit.

For $T > T_c$ a possible explanation of the observed behavior is that the magnetic interactions are not large enough to accomplish long-range magnetic order but short-range magnetic correlations are still present. The magnetic moments, which should be disordered by thermal energy, become frozen because the conditions for a three-dimensional spin glass are fulfilled, the local anisotropy overcomes the magnetic interactions imposing fixed directions at random for the magnetic moments. This situation remains up to the freezing temperature of 2 K, while at higher temperatures, a paramagnetic behavior is observed.

An alternative explanation of the situation described above could be a speromagnetism at low temperatures (below 1.1 K), with a ferromagnetic component along the b direction and a bidimensional spin-glass state in the (a,c) plane. The directions of these components are favored by magnetic interactions and crystal field, respectively, as discussed in Sec. III D. The $T_c = 1.1$ K corresponds to the Curie temperature for the b component, while the freezing temperature of the bidimensional spin glass is 2 K. Such state has been invoked several times in reentrant spin glasses although its existence is still controversial.[42] In fact, the speromagnetic state is predicted in the random magnetic anisotropy limit $D/J \gg 1$ (local anisotropy D larger than the exchange interactions J), which seems to be the case for $CeNi_{0.4}Cu_{0.6}$ at $T<T_c$ (Refs. 43 and 44).

Both models are consistent with the existence of the Kondo effect. However, the bidimensional spin-glass situation partly accounts by itself for the reduction of the magnetic moment deduced from neutron diffraction, where only the b component could be observed. Our present results do not allow us to distinguish between both situations.

The simultaneous effects of all the interactions produce such fruitful phenomenology in this compound, in which the CEF effects play also a crucial role; first, leading to a doublet ground-state split by the Kondo effect, far from the other excited doublets, turning the $S=\frac{1}{2}$ mean-field model into a useful approach to the Kondo lattice behavior; second, lead-'ing to a strong local anisotropy, which originates narrow domain walls in the ferromagnetic phase, and is in addition at the origin of the spin freezing. These CEF effects are often not considered in the analysis of Kondo and heavy fermion compounds but its importance is clearly demonstrated here. We think that the phenomenology presented in this work should not be a ''particular case'' but a more general situation in local low-symmetry compounds. The existence of the spin freezing phenomena, once the interactions are not important enough to impose the magnetic order (vicinity of the crossover localized-delocalized behavior), should be considered in close relation with other anomalous behaviors as the non-Fermi liquids.

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