Phase diagram of the $CeNi_{1-x}Cu_x$ Kondo system with spin-glass-like behavior favored by hybridization

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We present the magnetic phase diagram of the Kondo (ferromagnetic and antiferromagnetic) $CeNi_{1-x}Cu_x$ series revealing the existence of a ''spin-glass-like'' state above the Curie temperature T_C. The stability temperature range of this magnetically disordered phase increases when approaching the magnetic localized-delocalized crossover point ($x\approx 0.1$). This phenomenology is first discussed considering a classical model of spin-glass phase diagram including the effect of Kondo interactions. The similarities to the scenario described by recent theoretical analysis of strongly correlated electron systems, considering disorder and competing Ruderman-Kittel-Kasuya-Yosida and Kondo interactions, are also pointed out.

I. INTRODUCTION

The competition of interactions in strongly correlated f-electron systems is attracting a great deal of interest because of the physics involved: Kondo lattice, heavy fermions, and recently non-Fermi liquids (NFL's) or quantum phase transitions at zero temperature.[1,2] An adequate way to approach the problem is to study a system where the competition between the different interactions, needed to induce *a priori* those behaviors, could be modified by a single parameter: this is the case of $CeNi_{1-x}Pt_x$ (Ref. 3) and $CeRu_2Ge_2$ (Ref. 4) both evolving from ferromagnetism to Fermi-liquid behavior by changing composition or pressure, respectively, or the well-known $Y_{1-x}U_xPd_3$ (Ref. 5) and $CeCu_{5.9}Au_{0.1}$ (Ref. 6) systems which are some of the paradigmatic NFL's. Additionally, an increasing number of authors are referring to the relevance of disorder effects[7,8] in the low-temperature thermodynamic and magnetic properties of these substitutional strongly correlated systems and they find ground states such as spin-glass ones induced by structural disorder or random competing interactions. In such a way, recent experimental research on the ground state of the $CeNi_{0.4}Cu_{0.6}$ compound[9] shows that this Kondo lattice compound, with low local symmetry, presents a simple collinear ferromagnetic long-range order below $T_C=1.1$ K with the magnetic moments lying in the **b** direction. In addition, from all the measured bulk properties a spin-glass (SG) state below $T_f=2$ K is found, while at higher temperatures the compound becomes paramagnetic. In this context the general $CeNi_{1-x}Cu_x$ series presents many noticeable features, providing a singular and attractive system to investigate the competition of the different involved interactions, i.e., indirect [Ruderman-Kittel-Kasuya-Yosida (RKKY)] exchange interactions, large $4f$-conduction-band hybridization (Kondo) and strong crystalline electric-field (CEF) local anisotropy combined with the presence of disorder effects.

The previously obtained results for $CeNi_{1-x}Cu_x$ compounds[10,11] are summarized in Fig. 1. The stability domain of the orthorhombic FeB-type structure (Pnma) extends for $1\geqslant x\geqslant 0.2$. CeNi is CrB type (Cmcm). Both structures differ only in the relative disposition of trigonal prisms. A change from antiferromagnetism (AFM) for CeCu and $CeNi_{0.1}Cu_{0.9}$ to ferromagnetism (FM) for $x\leqslant 0.8$ is observed, as in other $R\mathrm{Ni}_{1-x}\mathrm{Cu}_x$ series.[12] Simultaneously, the $4f$-conduction-band hybridization increases with the Ni content, evolving in a similar way to that in the much studied $CeNi_{1-x}Pt_x$ series.[3] The stronger hybridization effects appear on the Ni-rich side, with CeNi being an intermediate valence compound. Consequently, these $CeNi_{1-x}Cu_x$ compounds are

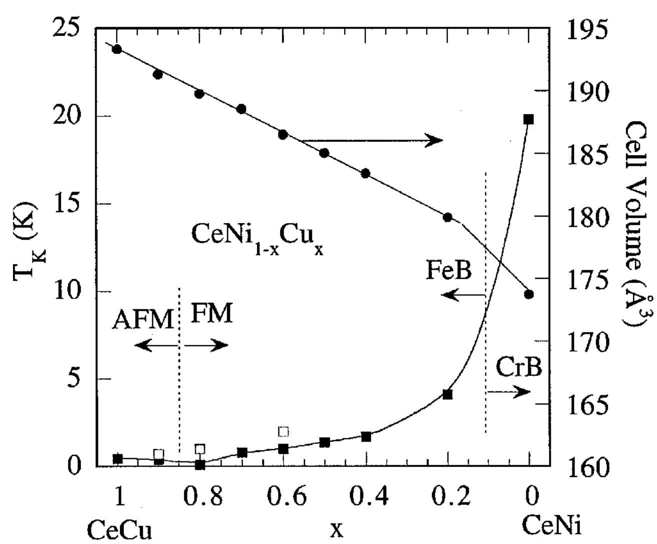

FIG. 1. Concentration dependence of the cell volume (full circles) and the Kondo temperature estimated from different techniques: magnetic susceptibility ($|\theta_p|/10$, full squares), quasielastic neutron scattering (QENS, open squares) for the $CeNi_{1-x}Cu_x$ series. The broken lines separate the FeB-CrB crystallographic structures and AFM-FM magnetic states. Full lines are guides for the eyes.

an interesting example of the few FM Kondo systems. It is worth mentioning that the crossover from the localized to the delocalized regime is defined around $x \approx 0.1$. In addition to this vast phenomenology, the observation of a SG-like freezing above the ordering temperature in $CeNi_{0.4}Cu_{0.6}$ compound[9] impels us to extend the search for SG behavior to the whole series. The aim of the present article is to present the phase diagram arising from that research, to discuss the role of the mentioned interactions, and to provide a scenario for future tuning of the theoretical approaches.

II. SAMPLES CHARACTERIZATION AND EXPERIMENTAL DETAILS

The studied compositions were those with $x=0.2$, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1. X-ray and neutron diffraction confirmed the same FeB-type orthorhombic structure for all the samples. The neutron-diffraction data ascertain a random Ni/Cu distribution on the 4c transition-metal site. The cell volume as well as the Ce-Ce and Ce-(Ni/Cu) next-nearest-neighbor distances increase continuously through the series, with increasing Cu content (see Fig. 1). The Rietveld refinement of both x-ray and neutron patterns gives in all the cases Bragg accuracy factors better than 9%. Only very small traces (<3%) of the $CeCu_2$ impurity phase were detected for the two Cu richer compositions ($x=0.9$ and $x=1$). The macroscopic homogeneity of the samples was checked by x-ray dispersive analysis (XDA). For each sample the same proportion of the constituents was obtained in different selected areas.

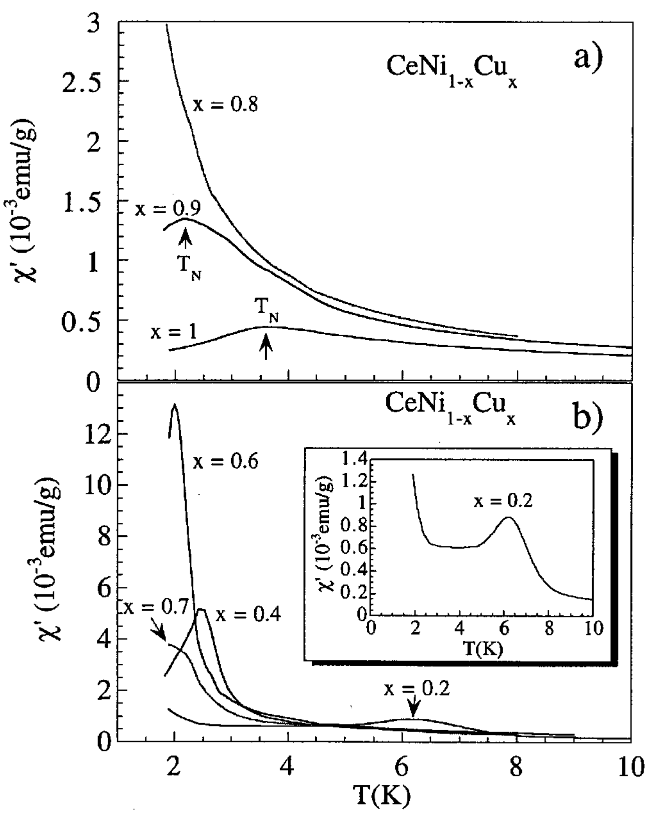

FIG. 2. Real part of the ac magnetic susceptibility χ_{ac} at $\nu=100$ Hz and zero applied magnetic field as a function of temperature for the $CeNi_{1-x}Cu_x$ compounds. (a) Antiferromagnetic compounds $x=0.9$ and $x=1$. (b) $x=0.2$ and ferromagnetic compounds: $x=0.4$, 0.6, 0.7, and 0.8. Inset shows the detail of $x=0.2$. Note the different susceptibility scales in figures (a) and (b).

III. χ_{ac} AND MAGNETIZATION RESULTS

ac susceptibility measurements χ_{ac} and their frequency and field dependence, magnetization measurements up to 9 T, as well as the analysis of the low-field magnetization in field cooling (FC) and zero-field cooling (ZFC) have been performed for all the studied samples, down to 1.8 K, in a PPMS (Quantum Design) magnetometer. The amplitude of the driving field H_{ac} was 1 Oe and the temperature was regulated to 0.01 K. In addition, magnetization loops and relaxation time measurements (after ZFC, a 0.5-T field was applied for 5 min and switched off at $t=0$) have been performed in the Ni-rich samples.

In Fig. 2, the real part of the ac susceptibility χ at $\omega=100$ Hz measured in zero applied field is presented as a function of temperature. For CeCu the maximum at 3.7 K corresponds to the Néel temperature T_N and for $CeNi_{0.1}Cu_{0.9}$ a similar behavior ($T_N=2.3$ K) is found [Fig. 2(a)]. The

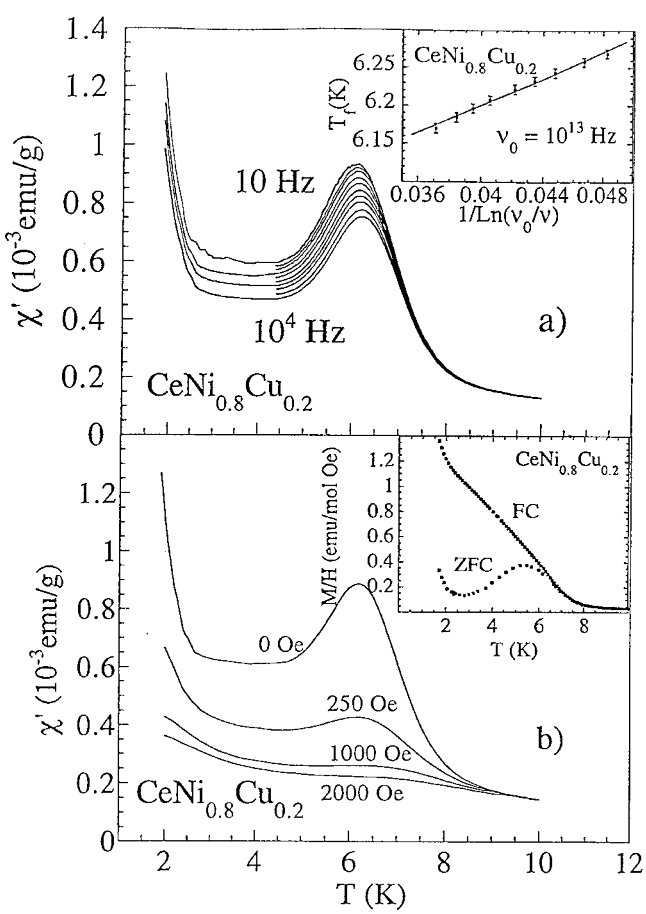

FIG. 3. (a) Real component of the ac magnetic susceptibility as a function of temperature measured at different frequencies for $CeNi_{0.8}Cu_{0.2}$. Inset shows the frequency dependence of the temperature maximum T_f, the line fits the Voguel-Fulcher law. (b) Real component of the ac susceptibility ($\nu=100$ Hz) as a function of temperature measured at different applied fields for $CeNi_{0.8}Cu_{0.2}$. Inset shows the field-cooled and zero-field-cooled magnetization vs temperature with a field of 100 Oe.

magnetization curves show below T_N a transition with the magnetic field (0.65 T for $x=1$ and 0.1 T for $x=0.9$ at 2 K). The FM compounds $0.4\leqslant x\leqslant 0.7$ [Fig. 2(b)] show an increase of the susceptibility at low temperatures, reaching a maximum which does not correspond to the T_C and their magnetization curves down to 2 K are paramagnetic [as for the previously reported $CeNi_{0.4}Cu_{0.6}$ (Ref. 9)]. The $CeNi_{0.8}Cu_{0.2}$ compound, where long-range magnetic order was not detected down to 1 K, presents the smallest susceptibility (except, of course, for AFM CeCu) but a broad maximum is observed, centered at 6 K [see inset Fig. 2(a)]. As a trademark of the behavior found for compounds with $x\leqslant 0.7$, we present in Fig. 3 the frequency and magnetic-field dependence of the χ_{ac} for $CeNi_{0.8}Cu_{0.2}$. The position of the maximum at 6 K shifts to higher temperatures with increasing frequency [Fig. 3(a)] and the anomaly is strongly reduced by the application of a weak magnetic field [Fig. 3(b)]. Accordingly, the imaginary part of χ_{ac} follows the same frequency and field dependence. A similar χ_{ac} behavior was observed for the FM compounds ($x\leqslant 0.7$). These maxima are associated with a SG-like freezing below T_f, defined as the temperature of the χ_{ac} maximum. For the AFM Cu-rich compositions ($x\geqslant 0.9$), the maximum corresponding to the T_N does not present any frequency shift and is unaffected by the application of a magnetic field up to 2 kOe and we have not observed any anomaly in χ_{ac} which could be attributed to a SG transition.

The frequency shifts of the maxima in the χ' susceptibility yield ratios $\Delta T_f/[T_f\cdot\Delta(\ln\nu)]$, ranging from 0.004 to 0.006, which are in good agreement with values previously reported for metallic glasses.[13] Furthermore, the $\nu(T_f)$ dependence follows the Vogel-Fulcher law [see inset of Fig. 3(a)] characteristic of a SG behavior,[13,14]

$$\nu=\nu_0\exp\left[-\frac{E_a}{T_f-T_0}\right],$$

which, considering a typical constant value of $\nu_0=10^{13}$ Hz,[14] permits us to estimate E_a and T_0, the obtained values are consistent with those reported for metallic spin glasses. The FC and ZFC magnetization data shown in the inset of Fig. 3(b) for $CeNi_{0.8}Cu_{0.2}$, as an example of such behavior, confirm that the spin freezing point corresponding to the M/H irreversibility appears in this compound at 6 K (for 100 Oe). However, the shape of the FC magnetization shows no plateau as usually occurs for the canonical spin glasses. Similar FC and ZFC behaviors have been found in random anisotropy systems[15] and reflect complex magnetic arrangements usually named ''speromagnetism'' and are considered as analogous to the SG in amorphous systems. This consists of frozen magnetic moment aggregates, randomly distributed and oriented, leading to a total zero magnetization.[16] In order to obtain a deeper characterization of this behavior, magnetization loops at different temperatures have been measured. Below T_f a small hysteresis is detected, and the area of the cycle increases when the temperature is lowered. The relaxation time measurements prove that the decay time of the isothermal remanent magnetization is drastically increased below T_f. The combined χ_{ac} and magnetization results presented here represent a qualitative but unambiguous description and firmly establish the SG-like behavior of these compounds below T_f. As a complement to these macroscopic measurements, further neutron static and dynamic experiments would be required to characterize the aggregates microscopically and they are already in progress.

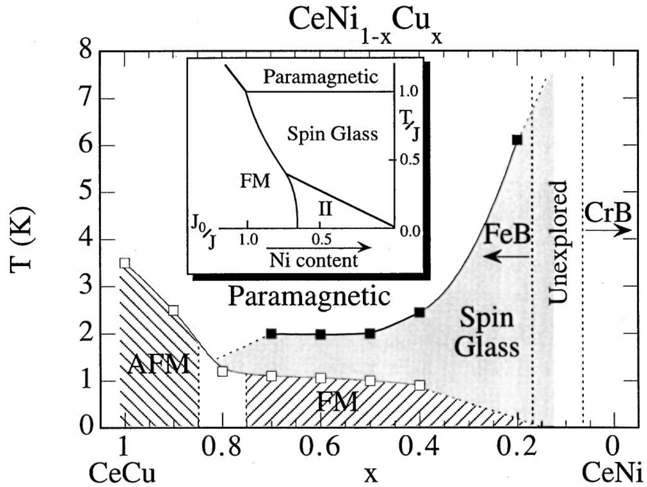

FIG. 4. Magnetic phase diagram for the $CeNi_{1-x}Cu_x$ series as a function of Cu concentration, where open squares represent the long-range magnetic ordering temperature $T_{C,N}$ and full squares represent the spin-glass freezing temperature T_f. Inset: Van Hemmen classical phase diagram proposed in Ref. 19. The arrow shows the direction of the displacement for increasing Ni content to help the comparison with the experimental diagram.

IV. PHASE DIAGRAM AND DISCUSSION

From these results we can propose the ground-state phase diagram represented in Fig. 4. The *a priori* conditions for the existence of a SG-like state were discussed in detail in Ref. 9, where the competing (positive and negative) exchange interactions and the disorder in the Ni/Cu nonmagnetic sites favoring an almost random anisotropy were considered. Furthermore, this Ni/Cu disorder locally influences the polarization of the conduction band leading to an additional disorder of the magnetic interactions.

Let us discuss now the proposed magnetic phase diagram, which is highly illustrative of the role played by the different interactions and the detailed competition between them. In the AFM CeCu limit, the mostly negative magnetic interactions are strong enough to establish a well-defined long-range antiferromagnetic structure.[17] For these Cu-rich compounds (which have the larger interatomic distances) no indications of Kondo effect are found. When we substitute Ni for Cu an increase of the $4f$-conduction-band hybridization and a change in the magnetic character (AFM to FM) are observed. Therefore the Kondo effect in our series begins to be significant for the FM compositions. The Kondo screening greatly reduces the magnetic moment and the Curie temperatures are smaller than the Néel ones (see Fig. 4). For the FM compositions, although the magnetic interactions are weakened, they can still induce the long-range magnetic order below $\approx$1 K. This is favored by the existence of a small coherent anisotropy, as reported by Chudnovsky and Serota,[18] which in our case leads to a **b** easy magnetization direction.[9] For $T>T_C$ only short-range magnetic correlations are present and the reduced magnetic moments, which should be disordered by thermal energy, become frozen, giving rise to a SG-like state. In this temperature range the coherent anisotropy, which decreases strongly with rising temperature, becomes negligible and the remaining random anisotropy imposes local fixed directions for the magnetic moments. This situation remains up to the freezing temperature T_f above which a paramagnetic state appears.

It seems clear therefore that the existence of a SG-like state in this kind of compounds is favored by the strong hybridization effects which lower the magnetic exchange interactions, together with the preponderance of the random anisotropy. In this sense, we have carefully studied the isostructural compounds $NdNi_{1-x}Cu_x$ (Ref. 12) to find any resemblance. For this series (with no Kondo effect) the ordering temperatures are 20 times larger and no evidence of SG behavior was found in any composition and temperature range, strongly supporting the proposed relationship between SG and hybridization effects. It is important to note that in the $CeNi_{1-x}Cu_x$ series no signs of SG have been observed at the crossover point from AFM to FM ($x=0.8$). The competing exchange interactions, always existent throughout the series, are a necessary but not sufficient condition for the existence of a SG regime, and it is not the ''competition'' itself but the reduced magnitude of the interactions due to Kondo effect that favor in this case the SG-like state.

The most striking fact of the magnetic phase diagram of the $CeNi_{1-x}Cu_x$ series (Fig. 4) is the increase of the SG stability range (T_f-T_C) for the Ni-rich compositions. A phenomenological relation $T_f-T_C \propto D/J$ could be proposed, where D represents the random anisotropy and J the exchange magnetic interactions ($H_{exch}=-JS_iS_j$). Assuming that D magnitude varies more slowly than J through the series, J is the driving parameter and while it is reduced due to the increasing Kondo effect ($x<0.5$), the SG existence range increases; this corresponds to the tendency observed in the phase diagram and indicates the coincidence of the larger SG stability range when approaching the crossover from localized to delocalized magnetic behavior. It is worth mentioning that the D/J ratio has usually been evoked as the tuning parameter to discuss the complex magnetic states (SG, cluster glass, speromagnetism, etc.) in amorphous systems.[16] In particular, for $D/J \gg 1$, the above commented speromagnetic state is predicted. It is well described that in correlated spin-glass systems[18] this arrangement should develop a macroscopic ferromagnetic component ($M\neq 0$) favored by the rise of the coherent anisotropy as commented above. It seems that this SG-like state acts as a precursor of the ferromagnetism, which tends to be established when the temperature is lowered.

The next point to be discussed is the comparison of our experimental phase diagram with the theoretical ones. Early in the 1980s J. L. van Hemmen[19] proposed a classical spin-glass model considering a *weakly correlated disorder* (long distances between magnetic impurities and then small magnetic interactions), with randomness in the interactions (considered as RKKY) and frustration. Four phases were obtained depending on the values of the dimensionless J_0/J and T/J parameters, where J is the total nearest-neighbor interaction while J_0 represents the ferromagnetic counterpart. The theoretical phase diagram is presented in the inset of Fig. 4. From this picture we can find a low-temperature ferromagnetic or mixed phase (coexisting FM and SG) that will evolve into SG for increasing temperatures, before becoming paramagnetic, which is clearly reminiscent of our experimental data for $x<0.7$ when ferromagnetic behavior is observed. The Kondo interactions could be considered as the mechanism leading to ''small magnetic interactions'' due to the increasing reduction of the local magnetic moments, which means ''*weakly correlated system*'' in the classical language and which is the first condition of the model. In our system, once the ferromagnetic interactions are predominant ($x<0.7$), the increasing Ni content induces higher hybridization, progressively reduces the strength of the magnetic interactions, and then, a larger temperature stability range of the SG phase appears (see Fig. 4). The existence of a mixed phase (SG and FM), as appears in the van Hammel diagram and already mentioned in Ref. 9, should not be discarded from the present magnetic measurements.

This old classical model provides only a qualitative explanation of the experimental phase diagram and the discussion must focus upon the present situation for spin glasses in strongly correlated electron systems. The existence of a SG regime does not seem to be an unusual case in strongly correlated electron systems (SCES's), e.g., U_2PdSi_3 (Ref. 20) or URh_2Ge_2 (Ref. 21) and the $Y_{1-x}U_xPd_3$ system[5] for ($x \approx 0.3-0.5$), among many others. Theoretical phase diagrams for metallic spin glasses in SCES's (Refs. 22 and 23) deal with the behavior close to the near zero quantum critical point, but in the present paper we cannot discuss the very low-temperature behavior, where quantum effects should predominate, because it needs a different set of measurements on selected compositions close to the localized-delocalized crossover point ($x\approx 0.8$), which are now in progress. However, we cannot overlook the fact that the scenario proposed here is absolutely reminiscent of recent analyses in a framework incorporating the essential aspects of the problem: competition between RKKY and Kondo interactions in the presence of magnetic anisotropy and disorder,[24] which is the situation of our system. These theories related to the so-called''Griffiths phase'' describe inhomogeneous situations with two coexisting phases, one of them behaving as a Fermi liquid (dominated by Kondo interactions) and the other with magnetically ordered regions (with predominant RKKY interactions). This situation seems to be represented in our series, as was discussed in the analysis of the experimental data. In fact, we have described the existence of aggregates with net local magnetization leading to a total $M=0$ (spin-glass-like or speromagnetism) which develops a $M\neq 0$ Ferromagnetic long-range order at lower temperatures for the $x=0.7$ to 0.4 compounds. This description represents the same idea underlying the Griffiths phases, especially for $CeNi_{0.8}Cu_{0.2}$, where aggregates coexist with an almost nonmagnetic matrix.

In conclusion, we propose the phase diagram of a series of compounds presenting hybridization effects, spin-glass-like behavior and different kinds of magnetic order. The system offers a vast phenomenology to quantitatively tune, in the future, recent theoretical approaches to the low-temperature regime and it is reasonable to think that the appearance of a SG-like state (speromagnetic or magnetic clusters leading to a total zero magnetization) could be a general feature existing close to the localized-delocalized crossover point in systems with strong random local anisotropy.

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