Evolution of magnetism and superconductivity in $CeCu_2(Si_{1-x}Ge_x)_2$

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We have determined the magnetic phase diagram of $CeCu_2(Si_{1-x}Ge_x)_2$ using specific heat, susceptibility, and resistivity measurements and additional thermal expansion and muon spin resonance experiments. The system evolves continuously from the heavy-fermion state at $x=0$ to an antiferromagnetically (AF) ordered state at $x=1$, though the magnetic structure undergoes significant modifications. The results strongly suggest that the AF ordering emerges from the A phase of pure $CeCu_2Si_2$. The phase diagram can be divided into three regions: Low Ge content ($x \leqslant 0.2$) leads to an enhancement of the A phase of pure $CeCu_2Si_2$ and to a moderate decrease of the Kondo temperature. Despite this increase of the magnetic character, we could observe superconductivity up to $x=0.1$. At large Ge content ($x>0.5$) the behavior resembles that of pure $CeCu_2Ge_2$. The intermediate region is characterized by the appearance of a second magnetic transition below T_N, which seems to be of first-order type. The appearance of this transition leads to a well-defined critical point at $x=0.3$ and suggests the possibility of another critical point at $x \simeq 0.5$. [S0163-1829(97)06425-4]

I. INTRODUCTION

Since the discovery of heavy-fermion superconductivity in $CeCu_2Si_2$,[1] this phenomenon has been the subject of intensive research. However, despite the large number of investigations, the origin and nature of this superconducting (SC) state remains unclear. In an earlier study, Rauchschwalbe suggested that the onset of SC is correlated to the disappearance of the magnetic ordered state.[2] The recent discovery of the onset of SC at the disappearance of the antiferromagnetic (AF) state in $CePd_2Si_2$ (Ref. 3) and $CeRh_2Si_2$ (Ref. 4) under pressure gives further support to this idea. More detailed investigations of $CeCu_2Si_2$ in the last years have, however, revealed a more complex behavior.[5,6] There is now clear evidence that besides the SC phase another phase, the A phase, may form below $T_A \simeq 0.8$ K in $CeCu_2Si_2$. This A phase shows up in the muon spin resonance (μSR) signal as a strong increase of the depolarization rate.[5] It is associated with pronounced anomalies in the temperature dependence of the ultrasound velocities, the thermal expansion, and a weaker anomaly in the specific heat.[6] Further, the onset of the A phase leads to a complete suppression of the NMR signal.[7] However, up to now, no clear related anomaly could be resolved in the magnetic susceptibility. Since the A-phase behavior in the NMR and μSR experiments do not correspond to any kind of classical antiferromagnetic order, its true nature has still not been established. This phase competes with the SC phase, as evidenced by its suppression at a temperature $T<T_c \simeq 0.7$ K, T_c being the SC critical temperature. Thus there is no coexistence on a microscopic scale between the magnetic and SC phases in pure $CeCu_2Si_2$, in contrast to the situation observed in uranium-based compounds.[8] In addition, slight deviations from stoichiometry were found to strongly affect the ground-state properties of $CeCu_2Si_2$. An excess of Cu stabilizes the SC phase, whereas an excess of Si stabilizes the A phase.[9]

Doping experiments are a powerful tool to get more insight into such a complex situation. The replacement of Si by isoelectronic Ge seems to be particularly well suited, because the change in the electronic states is expected to be rather smooth, allowing a detailed investigation. Since both compounds crystallize in the same $ThCr_2Si_2$-type structure, the main effect of Ge doping is related to its larger atomic size, resulting in an increase of the unit-cell volume, from $V \simeq 167$ Å^3 in $CeCu_2Si_2$ to $V \simeq 178$ Å^3 in $CeCu_2Ge_2$. In accordance with the expected decrease of the hybridization strength, $CeCu_2Ge_2$ presents AF order of localized moments at the Néel temperature $T_N = 4.15$ K.[10,11] The close relationship between the properties of both compounds is evidenced by x-ray diffractometry, resistivity, and nuclear quadrupole resonance NMR (NQR) measurements under pressure,[12,13] which show that $CeCu_2Ge_2$ at the critical pressure $P \simeq 7.0$ GPa (where it has the same volume as $CeCu_2Si_2$ at ambient pressure) presents the same physical behavior, including the transition from the AF to SC state.[14]

An earlier investigation of Ge-doped $CeCu_2Si_2$ revealed a discontinuous suppression of T_c, suggesting a pronounced drop between 3% and 4% at. % Ge.[15] In contrast, no studies were devoted to the evolution of the A phase at $x=0$ to the AF phase at $x=1$ until recently. We started a thorough investigation of this system by means of susceptibility, resistivity, specific heat, and thermal expansion measurements. Preliminary results, including a schematic phase diagram were presented in Ref. 16. A slightly different picture was proposed by Knebel *et al.*[17] on the basis of resistivity and susceptibility measurements, and using our early specific heat results. In this paper, we give a detailed report of our results. Using previous data of $CeCu_2Si_2$, $CeCu_2Ge_2$, and of the related compound $Ce(Cu_{1-x}Ni_x)_2Ge_2$ (Ref. 18) for comparison, we present a more precise analysis of the evolution of magnetism in $CeCu_2(Si_{1-x}Ge_x)_2$.

II. EXPERIMENT AND RESULTS

$CeCu_2(Si_{1-x}Ge_x)_2$ samples with compositions $x=0$, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.55, 0.6, 0.8, and 1 were prepared by melting the appropriate amount of pure elements in an arc furnace under an Ar atmosphere. After melting the samples several times to ensure homogeneity they were annealed, depending on the amount of Ge doping, between 700 °C and 1000 °C for approximately 120 h.[19] The samples were characterized by powder x-ray diffractometry using Si as an internal standard. No reflexes besides those belonging to the $ThCr_2Si_2$ structure were observed under a detection limit of 1.5% of the strongest 122 reflex. The exception is the $x=0.1$ sample, in which 2% of composition Ce_2CuSi_3 was detected, probably due to the peritectic formation of $CeCu_2Si_2$.

In contrast to the independent work presented in Ref. 17, which used Cu-rich specimens with composition $CeCu_{2.2}(Si_{1-x}Ge_x)_2$, all our results were obtained on stoichiometric samples since we found that Cu excess was incorporated in a large amount in the 122 phase.[20] Such an excess of Cu leads to significant changes of the structural and physical properties. The quality of the samples is evidenced, e.g., by the resistivity ratio $\rho_{300\,K}/\rho_{0.3K} \sim 20$ obtained in our $x=1$ sample, as discussed below.

Neither from x-ray patterns nor from the composition dependence of the residual resistivity measurements did we find any evidence of ordering of Ge and Si on the Si site of the tetragonal structure. Both lattice parameters a and c were found to increase almost linearly with Ge concentration as shown in Fig. 1 for some of the studied concentrations. This behavior indicates that the unit-cell volume also increases linearly with x as shown in Fig. 1(a), although there is a small deviation from linearity of the c/a ratio at high Ge concentration, as observed in Fig. 1(b). The fact that Vegard's law is verified for this system suggests that Ce valence is not affected in the whole concentration range.

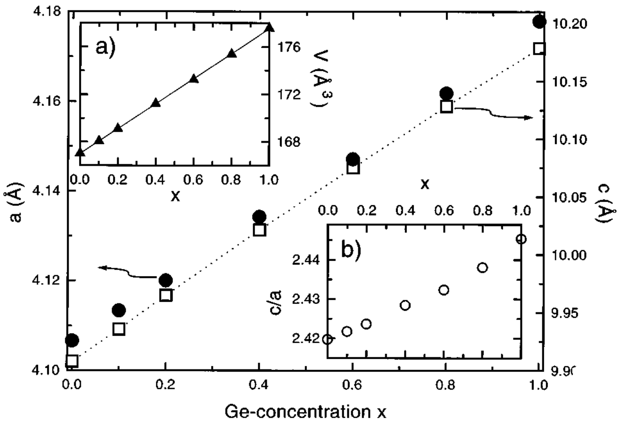

FIG. 1. Lattice parameters $a(\bullet)$ and $c(\square)$ of $CeCu_2(Si_{1-x}Ge_x)_2$ as a function of Ge concentration x. Insets: (a) unit-cell volume and (b) c/a ratio as a function of x. Lines are a guide to the eye.

The experiments were carried out using standard experimental techniques. The magnetic dc susceptibility was measured between 1.8 K and 300 K in a commercial superconducting quantum interference device (SQUID) magnetometer and the electrical resistivity with the standard four-probe ac technique. Some of the samples were studied by means of ac magnetic susceptibility between 0.4 and 20 K using a mutual-inductance bridge working at a fix frequency of 128 Hz. Specific heat was measured in a ^{3}He semiadiabatic calorimeter using the heat-pulse method between 0.4 K and 30 K in applied magnetic fields up to $B=4$ T. The thermal expansion was measured in a standard silver cell using the capacitance method in a dilution (^{3}He- ^{4}He) cryostat in fields up to 8 T. The resistivity and/or ac susceptibility of the Si-rich samples were also investigated down to 10 mK in a dilution cryostat, using standard techniques.

A. Electrical resistivity

The normalized resistivity $\rho/\rho_{T=300\,K}$ for the concentrations $x=0$, 0.1, 0.2, 0.4, 0.6, 0.8, and 1 is shown in Fig. 2 as a function of temperature. The overall behavior of $\rho(T)$ as a function of x agrees with previous results.[17] A high-

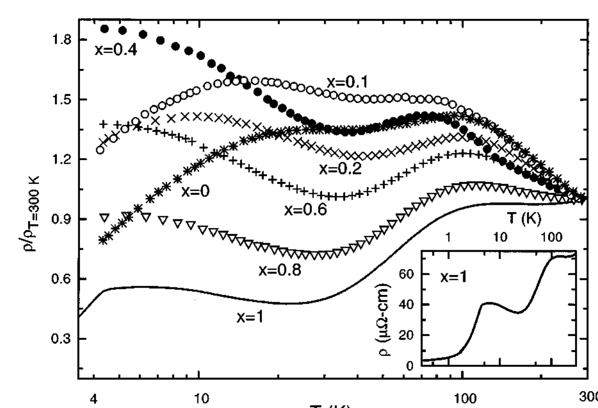

FIG. 2. Normalized resistivity $\rho/\rho_{T=300\,K}$ of some $CeCu_2(Si_{1-x}Ge_x)_2$ studied samples as a function of temperature. Inset: $\rho(T)$ for $CeCu_2Ge_2$ in a logarithmic scale.

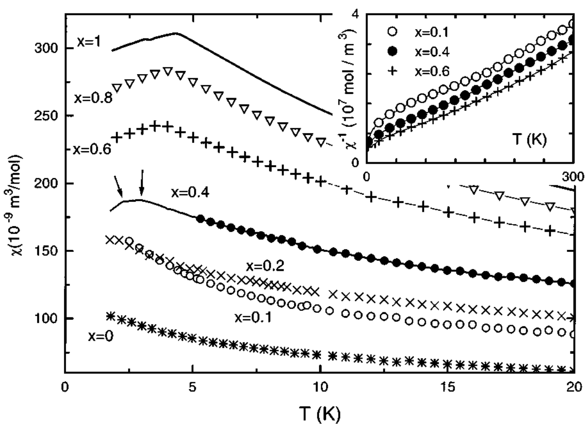

FIG. 3. Low-temperature magnetic susceptibility (χ) measured in $B=0.1$ T for some $CeCu_2(Si_{1-x}Ge_x)_2$ concentrations. The arrows indicate both transitions observed in $x=0.4$. Inset: high-temperature $\chi^{-1}(T)$ for $x=0.1$, 0.4, and 0.6.

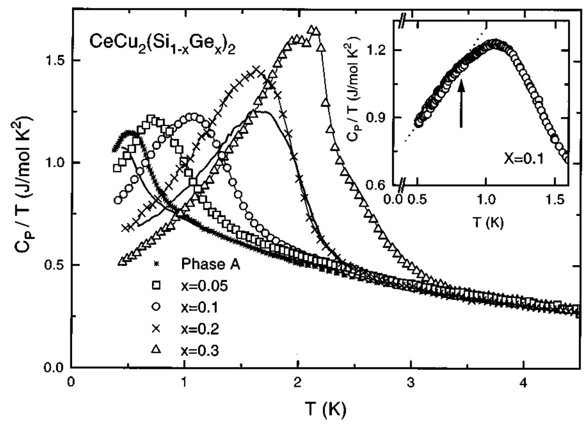

FIG. 4. Specific heat data of $CeCu_2(Si_{1-x}Ge_x)_2$, in the low concentration range as C_P/T vs T. The data for $x=0$ and 0.2 in $B=4$ T are represented by a solid line. Inset: detail of $x=0.1$ at low temperature showing the kink at 0.8 K.

temperature maximum at ~ 100 K reflects the effect of hybridization on the crystal-field excited levels of the Ce^{3+} ions. The fact that the position in temperature of this anomaly slightly depends on alloying indicates that the distribution of crystal-field levels is almost not affected by Ge concentration. At low temperatures, the maximum in $\rho(T)$ observed in the Si-rich samples reflects the Kondo interaction with the doublet ground state and the onset of coherence. The position of this maximum shifts from $T(\rho_{\max})\simeq 25$ K in pure $CeCu_2Si_2$ to less than 4 K at $x=0.4$. This clearly indicates a pronounced decrease of the hybridization strength with increasing x in this concentration range. As shown in Ref. 17, a kink appears in $\rho(T)$ around 2 K at $x=0.2$. This kink, which is related to the onset of magnetic order, gets more pronounced with increasing x and its position shifts to higher temperatures up to $T_N=4.35$ K in our $CeCu_2Ge_2$ sample. At $x=1$ we observe a decrease of one order of magnitude in $\rho(T)$ below T_N (see inset of Fig. 2).

B. Magnetic susceptibility

The temperature dependence of the dc susceptibility, $\chi_{dc}(T)$, for samples with $x=0$, 0.1, 0.2, 0.4, 0.6, 0.8, and 1 is shown in Fig. 3. For $x \geqslant 0.4$ the low temperature $\chi_{dc}(T)$ shows a kink corresponding to the presence of the AF transition. In this concentration range the values of $\chi_{dc}(T)$ and T_N increase with x approaching those of pure $CeCu_2Ge_2$.[11] It should be noticed that, whereas there is a single well-defined maximum for $x=0.6$, 0.8, and 1, two kinks are visible for $x=0.4$, indicating two magnetic transitions close in temperature. The increase in $\chi_{dc}(T)$ below 5 K for $x=0.1$ with respect to $x=0.2$ might be due to the presence of the Ce_2CuSi_3 phase detected in the crystallographic analysis of this sample.[19] In the inset of Fig. 3 the inverse of χ_{dc} deviates from a Curie-Weiss-like behavior below 200 K, probably due to the contribution of crystal-field levels, as reported by other authors.[21]

The AF character of the ordered phase for $x \geqslant 0.4$ samples was confirmed by ac susceptibility, χ_{ac}, results (not shown) in which the temperature of the maximum coincides with those observed in $\chi_{dc}(T)$. In the case of $x=0.4$ the lower transition (at ~ 2 K) observed in χ_{dc} corresponds to a strong increase of the χ_{ac} dissipative component, which suggests a change in the magnetic structure at this temperature and concentration.

C. Specific heat

The specific heat, C_P, results for the $x \leqslant 0.3$ composition range are shown in Fig. 4 as C_P/T vs T. The data for $x=0$ correspond to the nearly stoichiometric composition $Ce_{0.99}Cu_{2.02}Si_2$, which belongs to the A-phase existence regime of the $CeCu_2Si_2$ ternary phase diagram.[9] The reason for taking an A-phase sample as the $x=0$ limit for the $CeCu_2(Si_{1-x}Ge_x)_2$ system becomes clear by observing that for low ($x \leqslant 0.2$) Ge doping the $C_P(T,x)$ curves gradually develop from an A-phase shape. The broadened anomaly corresponding to A-phase formation at $x=0$ becomes more pronounced with increasing x and the transition temperature T_A (as determined from the temperature of the inflection point of the C_P/T data above the maximum) shifts to higher temperature, from $T_A=0.7$ K ($x=0$) to 1.95 K ($x=0.2$). In this range of Ge concentration there is a change in the $C_P(T)$ dependence below T_N, from $C_P \propto T^2$ at $x=0.1$ (see inset of Fig. 4) to $C_P \propto T^3$ at $x=0.3$ (not shown). As stated in Ref. 22 the comparison of C_P curves of different concentrations within $0 \leqslant x \leqslant 0.2$ clearly shows that the magnetic contribution corresponds to the condensation of nonmagnetic degrees of freedom described by a common $C_P/T \propto -\ln T$ curve.

The effect of magnetic field in C_P becomes weaker with increasing x, as included in Fig. 4. Whereas at $x=0$ a field of $B=4$ T shifts T_A by 20% to lower temperature and reduces the size of the anomaly, the same field on a $x=0.2$ sample has practically no effect on T_A, with a small reduction of the anomaly. Thus the increase of x leads to a significant stabilization of A-phase characteristics.

For $x=0.3$ a peaked structure appears at a temperature ($T_p=2.15$ K) slightly above the maximum in C_P, which indicates that around this concentration there is a qualitative change in the evolution of the magnetic structure of the sys-

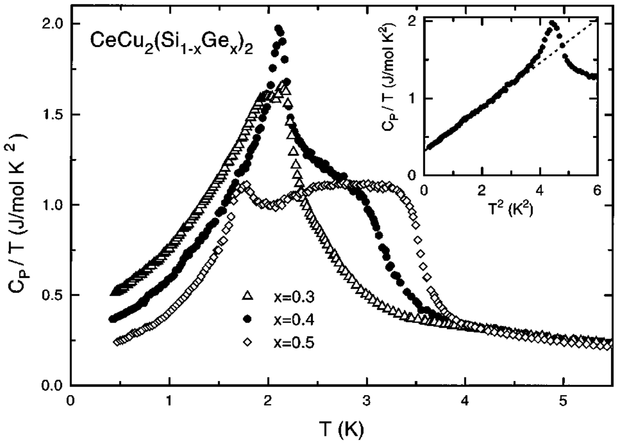

FIG. 5. Specific heat data of $CeCu_2(Si_{1-x}Ge_x)_2$ for intermediate concentrations in a C_P/T vs T plot. The inset shows the data for $x=0.4$ as C_P/T vs T^2, which evidences the T^3 dependence.

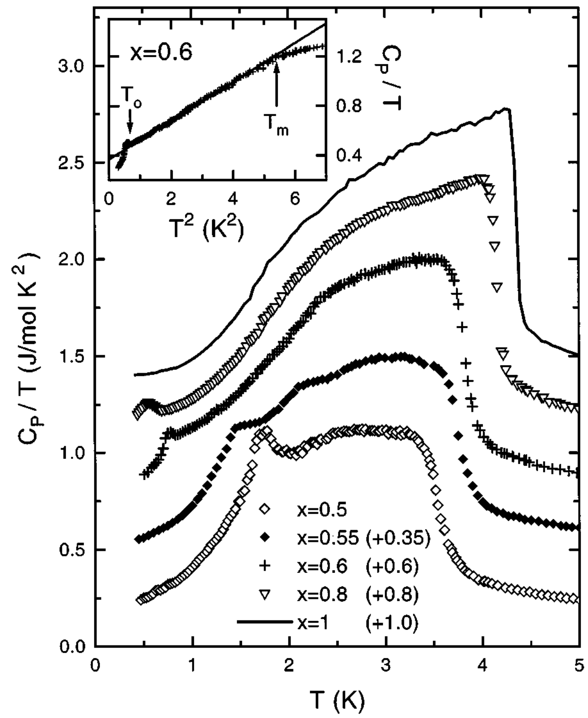

FIG. 6. Specific heat data of $CeCu_2(Si_{1-x}Ge_x)_2$, in the high-concentration range as C_P/T vs T. For clarity the curves are shifted vertically by the amount indicated in paretheses. Inset: $x=0.6$ data in a C_P/T vs T^2 plot where the $C_P \propto T^3$ dependence, the kink at T_m, and the anomaly at T_0 are evident.

tem. This is clearly seen in Fig. 5, where we compare the C_P/T data of the samples in the intermediate range of concentration. At $x=0.4$, the peak at $T_p=2.15$ K becomes very pronounced and it is accompanied by a shoulderlike anomaly at $T_N=3.2$ K. Both features correlate with the two maxima observed in $\chi_{dc}(T)$ (see Fig. 3). The arguments for interpreting this shoulder as the Néel transition are the AF-like anomaly in $\chi_{dc}(T)$ and its evolution with increasing Ge concentration. At $x=0.5$, the peak at T_p decreases again and is shifted to lower temperatures, whereas the shoulder evolves into a sharp mean-field-type anomaly and shifts to higher temperatures.

On the Ge-rich side the evolution of $C_P(T,x)$ is more continuous as shown in Fig. 6, where the C_P/T results for $x \geqslant 0.5$ are presented. The transition at T_N steepens further as a function of x and T_N increases from 3.55 K ($x=0.5$) to 4.35 K ($x=1$). Right above $x=0.5$, the peak at T_p evolves into two different anomalies. A peaklike one (at T_0) which shifts to lower temperature as x increases and disappears at $x=1$, and a second one at $T_m \simeq 2.3$ K which is almost independent of Ge concentration. This second anomaly gets broader for $x \geqslant 0.5$, transforming into a shoulder in C_P/T, which corresponds to the departure of the $C_P \propto T^3$ dependence as indicated in the inset of Fig. 6.

D. Thermal expansion

The temperature dependence of the thermal expansion, $\alpha(T)$, for $x=0$, 0.1, 0.2, and 0.4 is shown in Fig. 7. The $\alpha(T)$ results present a strong analogy to those of $C_P(T)$. The broad anomaly corresponding to the A-phase transition[9] for $x=0$ (at $T_A \simeq 0.7$ K) gets more pronounced and shifts to higher temperatures with increasing x. A small kink is visible at $T=0.8$ K in the $x=0.1$ curve, and for $x=0.4$ a pronounced notch appears, which is obviously related to the peak observed in the $C_P(T)$ results of Fig. 4.

We also include in Fig. 7 the results of thermal expansion in magnetic fields ($B=4$ T and 8 T) for $x=0.2$. The curves were obtained after zero-field cooling down to 0.2 K. The A-phase shape of the transition is almost unaffected by magnetic fields up to $B=8$ T whereas the transition shifts to lower temperature, from $T_A=1.95$ K in $B=0$ to 1.86 K and

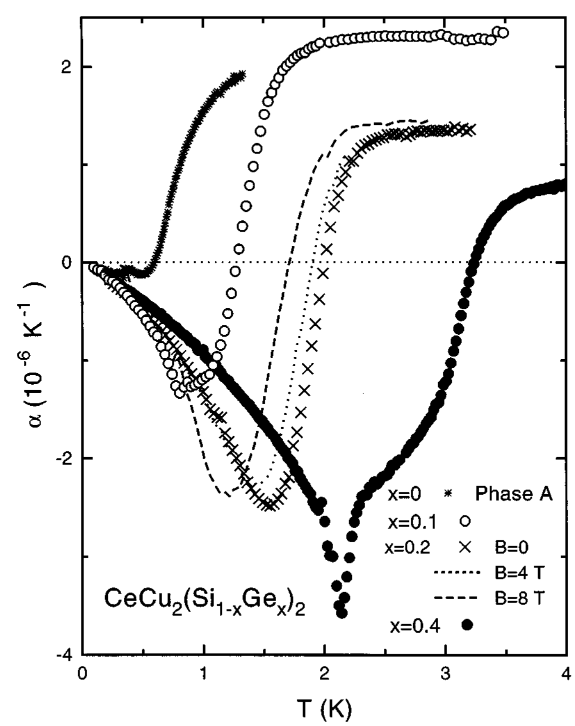

FIG. 7. Coefficient of thermal expansion as $\alpha(T)$ vs T at zero magnetic field. The dashed and dotted lines correspond to the $x=0.2$ sample in $B=4$ T and 8 T, respectively.

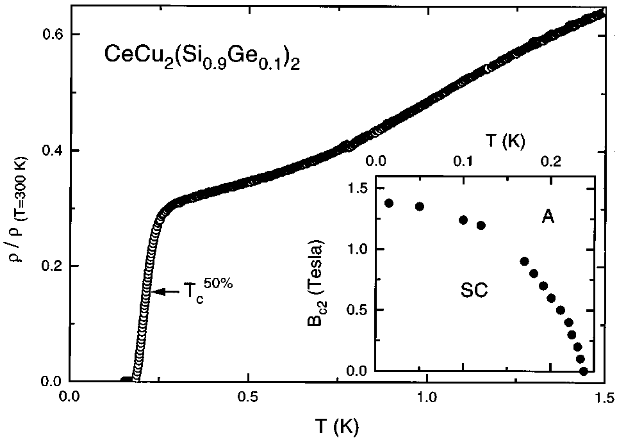

FIG. 8. Normalized resistivity $\rho/\rho_{T=300\,\mathrm{K}}$ for $x=0.1$ measured at zero field showing the SC transition at $T_c^{50\%}=0.21$ K. The inset shows the temperature dependence of the upper critical field B_{c2} separating the SC and A phases.

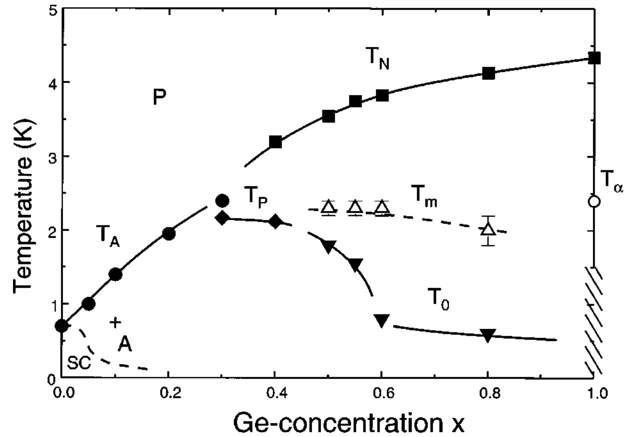

FIG. 9. (T-x) phase diagram of $CeCu_2(Si_{1-x}Ge_x)_2$. Temperatures T_A, T_N, T_p, T_m, T_0, and T_α are described in the text. P,A, and SC indicate paramagnetic phase, A phase, and superconducting phase, respectively. Solid symbols indicate well-defined transitions of a different nature and open symbols are related to a change of regime. Lines are a guide to the eye. The hatched region accounts for irreversibilities present in $CeCu_2Ge_2$ (Ref. 25).

1.55 K in $B=4$ T and $B=8$ T, respectively. Similar behavior is also observed for the $x=0.1$ sample in field (not shown), where the A-phase transition shifts to 1.15 K and 1.05 K in $B=6$ T and $B=8$ T, respectively.

E. Low-temperature resistivity and magnetoresistance in $CeCu_2(Si_{0.9}Ge_{0.1})_2$

In order to investigate the occurrence of SC in this system, we measured $\rho(T)$ of low-Ge-doped samples down to very low temperature (15 mK) and in applied magnetic fields up to 15 T. The zero-field resistivity for $x=0.1$ is plotted in Fig. 8 as $\rho/\rho_{300\,\mathrm{K}}$ vs T. A sharp SC transition is observed at $T_c^{50\%}=0.21$ K [defined as the temperature at which $\rho(T)$ is 50% of the value in the normal state] with a transition width $\Delta T=T_c^{90\%}-T_c^{10\%}=0.06$ K. The transition stays sharp in the magnetic field which allows us to determine the temperature dependence of the upper critical field $B_{c2}(T)$. At $T\rightarrow 0$ $B_{c2}(T)$ extrapolates to $B_{c2}(0)\simeq 1.5$ T whereas the value of the initial slope at T_c is $(dB_{c2}/dT)_{T_c}=-27$ T/K. These values are comparable to those of the SC phase of $CeCu_2Si_2$ (Ref. 2) and those reported for $CeCu_2Ge_2$ above the critical pressure,[14] which strongly suggest that SC at this Ge concentration is of heavy-fermion origin and intrinsic to the system. This is confirmed by preliminary C_P measurements that show a clear anomaly at 0.2 K. Superconductivity was also observed by χ_{ac} measurements in $x=0.05$ and $x=0.15$ samples at $T_c\simeq 0.2$ K and 0.1 K, respectively. The investigation of the SC as well as of the magnetic phase diagram in the low-Ge-doped samples will be presented in a forthcoming publication.[23]

III. DISCUSSION

As already pointed out, the results obtained by different kinds of measurements are quite consistent. These are included in a more detailed version of the temperature-concentration (T-x) phase diagram of $CeCu_2(Si_{1-x}Ge_x)_2$ displayed in Fig. 9, with substantial improvements compared to previous reports.[16,17] Although the variation of the transition temperatures T_A or T_N with Ge substitution is quite moderate and continuous, the magnetic structure undergoes significant changes. Two different types of behaviors, on the Si-rich and on the Ge-rich sides, are separated by an intermediate region at $0.3\leqslant x<0.5$, suggesting two critical points at $x=0.3$ and $x\simeq 0.5$. We now proceed to depict these distinct regions of the phase diagram in order to settle the main characteristics of the observed regimes.

At low Ge concentration ($x\leqslant 0.2$) the $C_P(T)$, and $\alpha(T)$ results show macroscopic A-phase-type features that enhance with increasing x. This strongly suggests that up to 20 at. % of Ge doping in $CeCu_2Si_2$ the A phase becomes more stable. For this reason the transition temperatures in this range of concentrations are labeled as T_A, instead of T_N, which characterizes the (paramagnetic) P-AF transition which occurs in the range $x\geqslant 0.4$. At zero field T_A increases with x by almost a factor $\sim$ 3, from 0.7 K ($x=0$) to 1.95 K ($x=0.2$). Simultaneously, the strength of the related anomalies at T_A in $C_P(T)$ and $\alpha(T)$ is enhanced by a factor of $\sim$ 3 and $\sim$ 2, respectively, and the entropy gain at T_N (see later on) increases by a factor $\sim$ 3 as well. The A phase is also stabilized with respect to the application of a magnetic field. Preliminary magnetoresistance measurements indicate an increase of the critical field of the transition from the A phase to the high-field phase[6,9] by a factor of $\sim$ 2.[23]

Further evidence of A-phase type of behavior is given by preliminary μSR results on $x=0.1$ and $x=0.2$ samples.[24] The signal observed in these samples resembles that of the A phase in pure $CeCu_2Si_2$. The onset of the strong depolarization related to the formation of the A phase shifts to higher temperature in agreement with the results of C_P and α measurements. The depolarization rate at $T\ll T_A$ increases linearly with the Ge content, from $\sigma\simeq$ 10 s^{-1} at $x=0$ to $\sigma\simeq$ 21 s^{-1} at $x=0.2$.[24] This indicates an enhancement of the size of the ordered moment. However, the analysis of the depolarization functions suggests a change from a fluctuating behavior in pure $CeCu_2Si_2$ to a more static character in the Ge-doped samples. Preliminary NMR measurements also suggest a change towards a static character of the magnetic phase with increasing Ge content.[23] Further μSR and NMR studies in the $0 \leqslant x \leqslant 0.2$ range are in progress in order to clarify the signatures of the magnetic phase and its evolution with Ge doping.

This low-Ge-content region ($x \leqslant 0.2$) is also characterized by the presence of a SC phase at low temperatures, as shown in the (T-x) phase diagram of Fig. 9. The extension of SC decreases as a function of concentration along with the enhancement of the A phase. At present new experiments are being carried out in order to establish the true relationship between these two phases at low x. For instance, a still open question is whether the competition between SC and the A phase, observed in pure $CeCu_2Si_2$ (Refs. 6 and 9), is also present in $CeCu_2(Si_{1-x}Ge_x)_2$.

The anomaly observed at 0.8 K in C_P and α in our $x=0.1$ sample lies within the A-phase region of the (T-x) phase diagram. A more detailed inspection of the measured data shows that it is related to the sudden departure from a $C_P \propto T^2$ dependence at that temperature, as indicated in the inset of Fig. 4. In this sense this anomaly might be connected with an incipient magnetic instability affecting the dispersion relation of the magnetic correlations. Preliminary measurements on another $x=0.1$ sample[23] show similar features with an even sharper anomaly at the same temperature. Further C_P, α, and ρ, as well as μSR experiments have been proposed in order to clarify this point.

At $x=0.3$ and (more pronounced) at $x=0.4$, a sharp anomaly in C_P and α is observed at the same temperature ($T_p = 2.15$ K), indicating a drastic change in the nature of the magnetic phase at this range of concentration. This is also evidenced in the temperature dependence of C_P at low temperature, which in the $x=0.4$ sample nicely follows a $C_P \propto T^3$ power law (see inset of Fig. 5) as expected for a classical antiferromagnet, in contrast to the $C_P \propto T^2$ power law observed for $x<0.2$ (see inset of Fig. 4). The drastic upward deviation from the T^3 law slightly below T_p and the sharpness of the peak at T_p in the $C_P(T)$ and $\alpha(T)$ data suggest a broadened first-order-type transition. The shape of this transition, its size, and the amount of entropy involved, $S \simeq 0.03R\ln 2$, are very similar to that observed in $Ce(Cu_{0.98}Ni_{0.02})_2Ge_2$.[18] In this alloy, the first-order character of this transition has been clearly demonstrated by $C_P(T)$ and $\alpha(T)$ measurements on single crystals.[25] Further, an anomaly at $T_p \simeq 2.2$ K was also observed in $\rho(T)$ measurements on pure $CeCu_2Ge_2$ under hydrostatic pressure at $P \geqslant 1.3$ GPa.[26] The replacement of Cu by Ni in $CeCu_2Ge_2$ corresponds to a strong change in the electronic states, whereas the substitution of Ge by Si or the application of external pressure should have only minor effect. Since the first-order transition at T_p can be induced in $CeCu_2Ge_2$ either by a very small doping with Ni or by a large doping with Si, this feature is probably related to tiny changes in nesting properties.

Other AF systems with a modulated magnetic structure also show such a sharp peak in C_P with similar values of entropy involved, as, for example, in $CeRh_2Ge_2$.[27] In this compound an incommensurate-to-commensurate transformation was explicitly proposed, but no evidence of a change of the propagation vector was reported from neutron scattering experiments.[28] Especially the comparison with $Ce(Cu_{0.98}Ni_{0.02})_2Ge_2$ shows that the first-order transition is closely related to the magnetism of pure $CeCu_2Ge_2$. Therefore we shall first analyze the results in the $0.5<x<1$ concentration range before discussing the first-order transitions at the intermediate concentration range.

The two anomalies emerging from the peak at T_p for $x \geqslant 0.5$ show very different qualitative behaviors. The transition temperature of the one at lower temperatures (T_0) decreases strongly between $x=0.55$ and $x=0.6$, but then remains almost constant for further increase of x. The shape of the C_P/T curve suggests a second-order-type transition. Since $C_P(T)$ for $T<T_0$ drops below the $C_P \propto T^3$ dependence extrapolated from the results for $T>T_0$ (see inset of Fig. 6), this transition seems to be related to the freezing of higher-temperature ($T \geqslant T_0$) magnetic degrees of freedom. On the other hand, the second anomaly at higher temperatures (T_m) has already broadened so much at $x=0.6$ that we cannot refer to it as a well-defined transition anymore. In any case, the changes in the curvature of C_P/T vs T at T_m suggest a change in the magnetic fluctuations regime (see inset of Fig. 6). Therefore this change of regime is represented by open symbols in the (T-x) phase diagram of Fig. 9. The concentration dependence of T_0 and T_m shown in Fig. 9 indicates that these two anomalies merge at $0.4<x \leqslant 0.5$, suggesting the presence of a critical point at this concentration. This might produce the drastic change in the magnetic structure that leads to the pronounced first-order transition at $x=0.4$. In this sense, one should notice the qualitative difference between the phase diagram displayed in Fig. 9 and that of Ref. 17. The anomalies below 1 K reported there for $0.2 \leqslant x<0.6$ are not observed in our $C_P(T)$ and $\alpha(T)$ results (cf. Fig. 4 and Fig. 7).

As $x \rightarrow 1$ both anomalies in C_P/T at T_0 and T_m become weaker and seem to vanish (Fig. 6). Even in our new $CeCu_2Ge_2$ sample with a significantly better resistivity ratio, and a sharper and higher transition temperature than in previous samples,[10,11] $C_P(T)$ exhibits only a weak maximum near $T_0 \simeq 0.5$ K without any evidence of a phase transition at T_m. Neither resistivity shows clear evidence of a transition (see inset of Fig. 2). However, recent $\alpha(T)$ results on a single crystal indicate a first weak anomaly at $T_\alpha = 2.4$ K and a strong irreversibility below $T \simeq 1.5$ K, indicating some instabilities of the magnetic structure at low temperatures.[25] Recent neutron scattering measurements suggest that the transition below 1.5 K is a lock-in transition to a commensurate structure, whereas no anomalous changes in the propagation vector were observed above 1.5 K.[29] A small reorientation of the moments cannot, however, be excluded from these neutron experiments, since the intensity of only a few reflexes have been recorded as a function of temperature. The same magnetic structure as that of $CeCu_2Ge_2$ at 1.5 K was observed for $x=0.8$ and $x=0.6$ at 1.6 K except for the decrease of the ordered moments and a slight change of the propagation vector.[17] As x is further decreased to 0.4 the intensity of the magnetic reflections are too weak to allow a clear analysis.[17] Further preliminary temperature-dependent neutron scattering experiments on the $x=0.6$ and $x=0.8$ samples indicate a change of the orientation of the moment between 1.5 K and 2.5 K.

All these results suggest that doping with a small amount of Ni or with a large amount of Si, or applying hydrostatic pressure $P>1.3$ GPa,[26] leads to the transformation of these instabilities to mean-field transitions. In $CeCu_2(Si_{1-x}Ge_x)_2$ these two related anomalies (at T_0 and T_m) merge around $0.4<x<0.5$, into one pronounced first-order transition, which itself merges with the Néel transition, leading to a well-defined critical point at $x\simeq0.3$. These changes in the magnetic structure are probably related to small changes in the topology of the Fermi surface. Clearly further neutron scattering experiments are needed to establish the nature of these transitions. Preliminary susceptibility measurements on single crystals show no change in the magnetic anisotropy in the whole concentration range, indicating that the pronounced changes in the magnetic structure cannot be due to changes in the anisotropy.

The question is now how this complex magnetic phase diagram is related to the evolution of the Kondo temperature T_K. A first indication is given by the low-temperature maximum in $\rho(T)$. As already discussed, the shift of $T(\rho_{\max})$ to lower temperature between $x=0$ and $x=0.4$ reflects a significant decrease of T_K in this concentration range. Around $0.3<x<0.4$, the strong decrease of $T(\rho_{\max})$ is connected with the appearance of the peak in C_P and α at T_p. Thus the concentration $x=0.3$, at the critical point in the (T-x) phase diagram, corresponds to the region where T_K and T_N (i.e., the energy scales for the on-site and intersite interactions) become comparable.

Further information can be obtained from the analysis of $C_P(T)$ and the $4f$ entropy gain $S(T)$ at T_N (or T_A). The γ values are obtained from the extrapolation of C_P/T to $T=0$ K. Using the same extrapolation, $S(T)$ was obtained by integrating C_P/T after the subtraction of the (almost negligible) phonon contribution. Between $x=0$ and $x=0.5$, γ strongly decreases as $S(T_N)$ increases, indicating that the fraction of degrees of freedom involved in the ordered state increases as well. Between $x=0.5$ and $x=1$, this increase is much weaker. In order to get more information we analyze the electronic contribution to C_P in terms of a single-impurity model[30] following the procedure of Ref. 10 for $CeCu_2Ge_2$. The data for $x=0.6$ and 0.8 are well fitted in the P range (up to ~15 K), getting an entropy balance at T_N between the single impurity $C_P(T)$ curve extrapolated to $T\to0$ and the experimental results. The extracted values for the fitting parameter T_K are 5.5 K ($x=0.6$) and 5 K ($x=0.8$), in coincidence with the values of $T(\rho_{\max})$.

The extrapolation of the fit to $T\to0$ leads to γ values one order of magnitude larger than those determined in the magnetic ordered state, implying that the Kondo effect is largely quenched by the magnetic ordering. This means that on the Ge-rich side an important fraction of the Kondo degrees of freedom condenses into the AF phase at $T<T_N$. From the ratio $T_K/T_N\simeq1.2$ the value of the specific heat discontinuity $\Delta C_P(T_N)\simeq5$ J/mol K can be estimated within a molecular field model,[31] in agreement with our experimental values (cf. Fig. 4).

For $x\leq0.3$ the single-ion $C_P(T)$ curve, fitted to the $T>T_A$ data, stays below the experimental results in the whole $T<T_A$ range, reaching the extrapolated γ value to $T=0$. As a result, no entropy balance is obtained at T_A. However, such a balance can be obtained using a $C_P\propto-T\ln T$ curve fitted to the $T>T_A$ results as discussed in Ref. 22. This fit suggests that magnetic fluctuations play a very important role in this concentration range.

All these results point to a significant decrease of T_K between $x=0$ and $x=0.5$ and only a weak decrease at larger Ge contents. This evolution of T_K has a strong analogy with the P-AF phase boundary of the magnetic phase diagram, which presents pronounced variations in the $0<x<0.5$ region, but only weak changes in the $0.5<x<1$ range.

IV. CONCLUSIONS

We have investigated the evolution of magnetism in $CeCu_2(Si_{1-x}Ge_x)_2$, by means of resistivity, susceptibility, specific heat, and thermal expansion measurements and additional μSR results. The system clearly evolves from the A phase of $CeCu_2Si_2$ to the classical (localized magnetic moment) AF state in $CeCu_2Ge_2$. The transition temperature of the ordered state was found to increase continuously from $T_A=0.7$ K in $CeCu_2Si_2$ to $T_N=4.35$ K in $CeCu_2Ge_2$, this increase being steeper on the Si-rich side than on the Ge-rich one. On the contrary, the evolution of the magnetic nature of the system was found to be very discontinuous. Our results indicate three different regimes: at low Ge content ($0\leq x<0.3$), intermediate content ($0.3\leq x<0.55$) and large x content ($0.55\leq x\leq1$).

At low Ge content ($x<0.2$) the (T-x) phase diagram shows the presence of the A phase and, at lower temperatures, a SC phase. The effect of doping is the enhancement of the A phase of pure $CeCu_2Si_2$, which might be associated with a change of the microscopic nature of this phase from a dynamic character at $x=0$ to a more static one in the Ge-doped samples. This stabilization of the A phase is also correlated with a pronounced decrease of the Kondo temperature in this concentration range.

The intermediate region is characterized by a pronounced peak in C_P/T at $T_p\simeq2.3$ K$<T_N$, which separates from the P-AF transition at $x=0.3$, leading to a critical point at this concentration. The $C_P(T)$ and $\alpha(T)$ results indicate that this peak corresponds to a first-order transition between two different magnetic structures. Our results further indicate that T_K and T_N become comparable in this concentration range. At the border between the intermediate- and high-Ge-content regions, the peak at T_p splits into two anomalies, which seem to correspond to two incipient instabilities in the magnetic structure of pure $CeCu_2Ge_2$: one at a higher temperature T_m (or T_α), related to a reorientation of the moments, and a second one at low temperature, related to a lock in of the propagation vector. In the high-Ge-content region, we observe a smooth evolution towards the behavior observed in $CeCu_2Ge_2$, without pronounced changes in the magnetic structure or in the Kondo temperature. These pronounced changes in the magnetic features are not due to changes of the anisotropy of the system, but seem to be related to tiny changes of the electronic states.

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