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Magnetic behavior of the Kondo-lattice system $CeRu_2Si_2$

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We demonstrate experimentally that the intermetallic compound $CeRu_2Si_2$ exhibits low-temperature magnetic properties similar to those of the heavy-fermion superconductor $CeCu_2Si_2$. Magnetic susceptibility and ^{29}Si nuclear magnetic resonance (NMR) measurements establish that the ground state of $CeRu_2Si_2$ is nonmagnetic, and electrical resistivity measurements reflect Kondo-type spin fluctuations. The observed proportionality between the Ce contributions to the ^{29}Si NMR shift K and the magnetic susceptibility χ distinguishes $CeRu_2Si_2$ from mixed-valence Ce- and Yb-based systems found previously to exhibit anomalous nonlinear dependence of K on χ.

Cerium-based intermetallic compounds with the $ThCr_2Si_2$-type tetragonal structure possess rather interesting physical properties. In the compounds CeT_2Si_2, where T is a $3d$ transition-metal atom (Mn through Cu), the lattice anomaly (departure of the lattice volume from that characteristic of the trivalent rare earths) decreases progressively upon passage from Mn to Cu.[1] This indicates a systematic variation of the Ce valence, from strongly mixed valent[2] (carrying no moment) in $CeMn_2Si_2$, to nearly trivalent[3] in $CeCu_2Si_2$. Compounds with $T=$Cu, Ag, Au, and Pd have been investigated and have been shown to exhibit a variety of phenomena. $CeCu_2Si_2$ appears to undergo a superconducting phase transition,[3] despite the fact that the Ce carries nearly its full magnetic moment at high temperatures,[4] and that the system exhibits the properties of a heavy Fermi liquid at low temperatures.[3] Electrical resistivity measurements indicate the presence of a moment instability in $CePd_2Si_2$,[5] as in $CeCu_2Si_2$,[6] but the absence of such an instability in $CeAu_2Si_2$.[5] On the other hand, magnetic susceptibility[5] and neutron-diffraction[7] measurements suggest the onset of antiferromagnetic ordering at $T_N \simeq 10$ K in both $CePd_2Si_2$ and $CeAu_2Si_2$.

Motivated in part by the search for other systems which exhibit heavy-fermion superconductivity, and for clues to the morphological and electronic properties required for this phenomenon, we considered it of interest to examine other members of the CeT_2Si_2 system. We present here the results of magnetic susceptibility, electrical resistivity, and ^{29}Si nuclear-magnetic-resonance (NMR) shift measurements on $CeRu_2Si_2$.

A sample was prepared by arc melting the pure constituents (99.99%-pure Ce, 99.999%-pure Si, and 99.9%-pure Ru) in an argon atmosphere. The button was flipped several times and remelted to achieve good homogeneity. The overall weight loss during melting was less than 1%. The room-temperature lattice constants of the well-crystallized sample, $a = 4.20$ Å and $c = 9.81$ Å, agree very well with those found in the literature.[8] X-ray diffraction powder patterns gave no indication of spurious phases within the resolution ($\sim 5\%$) of the technique.

The magnetic susceptibility was measured at ~ 1.5 kOe

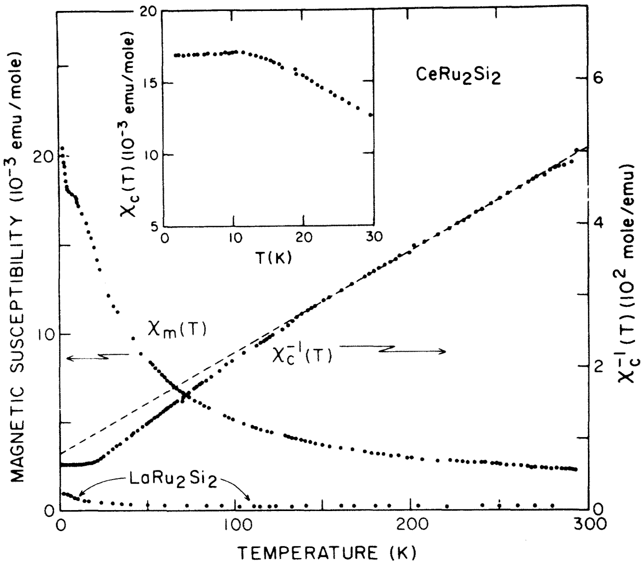

FIG. 1. Temperature dependence of the measured susceptibility $\chi_m(T)$ and inverse-corrected magnetic susceptibility $\chi_c^{-1}(T)$ of $CeRu_2Si_2$. See text for correction procedure. Dashed line: Curie-Weiss fit to corrected high-temperature data. Susceptibility of the reference compound $LaRu_2Si_2$ is also shown. Inset gives $\chi_c(T)$ below 30 K.

between 1.5 and 300 K using a Faraday balance. The electrical resistivity was measured between 1.5 and 300 K on samples vacuum-cast into suitable shapes (1 mm$^2\times$2 cm) and situated in helium gas. ^{29}Si NMR spectra were obtained for temperatures between 2 and 300 K using a pulsed spin-echo NMR spectrometer.[9]

The measured susceptibility $\chi_m^{(T)}$ is seen to increase monotonically from 300 to 4 K (Fig. 1), with a particularly slow rate of increase from 10 to 4 K. Below 4 K, χ_m exhibits a sharp rise with decreasing temperature, which is presumably due to a small contribution of stable-moment Ce ions situated on or near grain boundaries or other defects. After correcting for the impurity contribution,[10] and subtracting the susceptibility of LaRu$_2$Si$_2$ (also shown in Fig. 1), we obtain the corrected susceptibility $\chi_c(T)$ of Ce ions in CeCu$_2$Si$_2$. As seen from the plot of $\chi_c^{-1}(T)$ in Fig. 1, χ_c is of the Curie-Weiss form $\chi_c(T)=C/(T+\Theta)$ at high T, with $\Theta=54$ K and $\mu_{\text{eff}}=2.38\mu_B$. Below about 140 K the Curie-Weiss constant decreases with decreasing temperature, as has been previously observed in other Ce-based Kondo-lattice systems such as CeAl$_3$,[11] CeAl$_2$,[12] and CeCu$_2$Si$_2$.[13,14] Below about 10 K, χ_c ceases to depend on temperature (inset to Fig. 1). The presence of crystalline electric fields (CEF) cannot alone give rise to a temperature-independent susceptibility at low temperatures, because of the Kramers degeneracy of the Ce^{3+} ground state. The saturation of χ_c at low temperatures is therefore attributed to spin fluctuations arising from either Kondo or valence fluctuations, or a combination of the two. We can estimate the spin-fluctuation temperature T_{sf} at $T=0$ by noting that it typically scales with $C/\chi(0)$.[15] For CeRu$_2$Si$_2$ the value of $\chi_c(0)$ per mole Ce (Fig. 1) is approximately twice that of CeCu$_2$Si$_2$.[6] Assuming that the two systems have the same CEF ground state, we obtain $T_{\text{sf}}\sim 5$ K for CeRu$_2$Si$_2$, since $T_{\text{sf}}\sim 10$ K for CeCu$_2$Si$_2$ from quasielastic neutron scattering measurements.[13]

^{29}Si NMR shifts $K(T)$ were measured with respect to the ^{27}Al resonance in a saturated solution of AlCl$_3$, assuming the ratio of gyromagnetic ratios $\gamma(^{29}\text{Si})/\gamma(^{27}\text{Al})$ to be 8.458/11.094.[16] The temperature dependence of $K(T)$ is given in Figs. 2 and 3. The overall variation of $K(T)$ is from 0.10% at room temperature to 0.38% at 2 K. This variation is similar to that seen in CeCu$_2$Si$_2$,[14] viz., from 0.2% at room temperature to 0.6% at 2 K. The linewidth increases from $\sim$5 Oe at room temperature to $\sim$35 Oe at 2 K due, to a considerable extent, to unresolved structure arising from anisotropy of the NMR shift. Figure 2 gives $K(T)$ as a function of the corrected susceptibility $\chi_c(T)$, with the temperature as an implicit variable. Within the limits of experimental accuracy the shift is a linear function of the susceptibility. The measured shift is essentially independent of temperature below 10 K. This important feature is clearly seen in Fig. 3, where the temperature dependence of $\chi_c(T)$ and $K(T)$ are superimposed, with the ordinate for $K(T)$ shifted and scaled according to the linear relationship given in Fig. 2. The linearity of $K(\chi_c)$ and, in particular, the temperature independence of $K(T)$ at low temperatures, support our conjecture that the upturn of $\chi_m(T)$ below 5 K is indeed extrinsic in character, and hence justify the subtraction procedure for obtaining $\chi_c(T)$ discussed above. These results also clearly rule out the possibility of a magnetic phase at low temperatures, even if it were of a subtle topology which did not register dramatically, in the magnetic susceptibility, because such a phase would almost certainly give rise to a greatly increased NMR shift and/or linewidth.

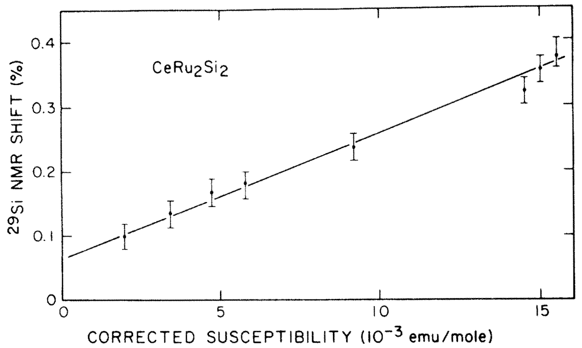

FIG. 2. Dependence of the ^{29}Si NMR shift $K(T)$ on corrected susceptibility $\chi_c(T)$ in CeRu$_2$Si$_2$, with temperature as an implicit parameter. Straight line is a least-squares fit to the data.

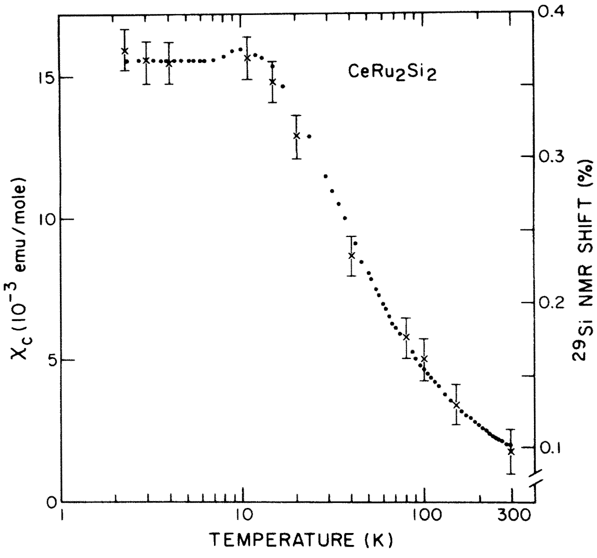

FIG. 3. Comparison of the temperature dependences of $\chi_c(T)$ (dots) and $K(T)$ (crosses). Zero of the scale of $K(T)$ has been shifted and the ordinate scaled corresponding to the linear dependence $K(\chi_c)$ shown in Fig. 2.

The fact that $K(T)$ is proportional to $\chi_c(T)$ implies that the transferred hyperfine field H_{hf} at the Si nucleus is essentially temperature independent. The magnitude of H_{hf} may be evaluated[16] from the relationship

$$K(T)=(H_{\text{hf}}/N\mu_B)\chi_c(T)\ ,$$

and is 1.1 kOe/μ_B. In CeRu$_2$Si$_2$ the saturated low-temperature susceptibility is roughly twice that of CeCu$_2$Si$_2$. The shift is smaller, however, corresponding to a smaller hyperfine field in CeRu$_2$Si$_2$. The linearity between K and χ_c observed for CeRu$_2$Si$_2$ distinguishes it from the weakly mixed-valent systems CeSn$_3$, YbAl$_3$, and

YbCuAl, for which K and χ are not proportional at low temperature.[17] This disparity in behavior may reflect either the relatively larger spin-fluctuation temperatures in the latter three systems, or some variation with temperature of the electronic states which determine the transferred hyperfine interaction.

A weak maximum in the corrected susceptibility at ~ 10 K can be seen in Fig. 1 and more clearly in Fig. 3. On the basis of our present results it is not possible to determine whether the maximum is a real effect, or an artifact of the subtraction procedure used to arrive at χ_c. Such maxima are frequently observed in mixed-valent materials at temperatures roughly equal to the characteristic spin-fluctuation temperature T_{sf}. They are also present even in the dilute Kondo problem, as revealed by a solution[18] of the exact thermodynamic equations of the Coqblin-Schrieffer model in the case $J > 1$, where J is the total angular momentum of the impurity spin. In the latter case the maximum occurs at roughly half the Kondo temperature. In discussing systems such as $CeRu_2Si_2$ or $CeCu_2Si_2$ it becomes an academic exercise to decide between Kondo behavior or weak mixed valence, since there is no clear method for distinguishing these experimentally. Nevertheless, we note that a low-temperature anomaly in $K(\chi)$ is observed in three systems, noted above, which are generally considered weakly mixed valent. This anomaly is weak in $CeCu_2Si_2$ (Ref. 14) and absent in $CeRu_2Si_2$.

The temperature dependence of the electrical resistivity of $CeRu_2Si_2$ is shown in Fig. 4. While the anomalous contribution from spin fluctuations is not as large as in the case of $CeCu_2Si_2$ (Ref. 6) and $CePd_2Si_2$, (Ref. 5) it is clearly evidenced as a negative curvature in the temperature range 2—40 K. This excess conductivity could be more clearly exhibited if it were possible to subtract the phonon contribution, which is expected to have positive curvature in the same temperature range. We have no explanation for the large difference between the magnitudes of the anomalous contributions to the low-temperature resistivities of $CeRu_2Si_2$ and $CeCu_2Si_2$.

Finally, we note that the results presented above establish $CeRu_2Si_2$ as a likely candidate for a heavy-fermion superconductor, since its properties are quite similar to those of $CeCu_2Si_2$. This is not the case for other members of the CeT_2Si_2 series. One sample of $CeRu_2Si_2$ was examined for superconductivity using an ac susceptibility technique. No transition was found down to 0.040 K, whereas the superconducting transition in $CeCu_2Si_2$ occurs at $T_c \sim 0.6$ K.[3] Recent detailed studies[19] have established, however, that the superconducting state of $CeCu_2Si_2$ is extremely sensitive to stoichiometry and alloying. Vacancies or impurities at the level of a few percent on the Cu sublattice depress T_c by an order of magnitude. These results motivate continuation of the search for superconductivity in $CeRu_2Si_2$ samples designed to ensure the integrity of the Ru sublattice; e.g., off-stoichiometry samples with a Ru excess.

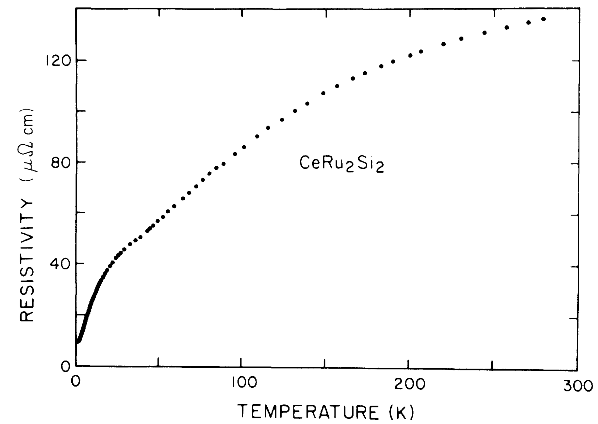

FIG. 4. Temperature dependence of the electrical resistivity of $CeRu_2Si_2$.

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