Magnetic phase transitions in $CeRh_2Si_2$: Specific heat, susceptibility, and resistance studies

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Two phase transitions near 35 and 24 K can be detected in the specific heat, susceptibility, and resistivity of $CeRh_2Si_2$. We interpret the 35 K transition as magnetic ordering in a $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ structure. The much weaker transition near 24 K corresponds to the development of domains having a $(\frac{1}{2}\ \frac{1}{2}\ 0)$ magnetic structure that grow spatially at the expense of the $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ structure. This interpretation of the magnetic phase diagram of $CeRh_2Si_2$ clarifies a controversy surrounding observations by neutron diffraction. [S0163-1829(98)06714-9]

The isomorphic system $Ce(Ru_{1-x}Rh_x)_2Si_2$ shows a very rich electronic and magnetic phase diagram as a function of the concentration x and the applied pressure P. It exhibits a variety of behavior, including long-range magnetic ordering for $x>0.5$,[1] heavy-fermion character,[2,3] metamagnetic and spin-density-wave transitions[4–6] and superconductivity for $x=1$ at high pressure.[7] A common view is that this broad range of phenomena originates from tuning the hybridization between the f and conduction electrons by varying x or P, or, expressed in Doniach's model[8] from the competition between Kondo and Ruderman-Kittel-Kasuya-Yosida interactions. In a recent study we have compared pressure with concentration tuning and demonstrated that near the critical point at the zero-temperature magnetic-nonmagnetic boundary ($x=1$, $P_c \geqslant 9$ kbar, or $x_c=0.5$, $P=0$) local ligand disorder plays an important role in producing non-Fermi liquid $-\ln T$ behavior in the specific heat and magnetic susceptibility.[9]

Interestingly, the precise nature of local-moment magnetism in the end compound $CeRh_2Si_2$ at zero pressure has remained unclear in spite of rather thorough study. From analysis of neutron-diffraction measurements on polycrystalline $CeRh_2Si_2$, Grier *et al.*[10] proposed two antiferromagnetic structures with ordering temperatures $T_N^u=39$ K and $T_N^l=27$ K. Magnetic peaks for $T_N^l<T<T_N^u$ were indexed to a $(\frac{1}{2}\ \frac{1}{2}\ 0)$ magnetic structure; whereas, below T_N^l additional peaks corresponding to $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ appeared. However, these authors could not determine unambiguously whether these two magnetic structures coexisted homogeneously or inhomogeneously throughout the sample volume. In either case, the calculated ordered moment was greater than the maximum of 2.14 μ_B allowed by crystal-field splitting in tetragonal symmetry. On the other hand, Quezel *et al.*[11] observed only a single antiferromagnetic transition at 36 K with a magnetic structure of $(\frac{1}{2}\ \frac{1}{2}\ 0)$ and an ordered moment of 1.50 μ_B. More recent single-crystal neutron-diffraction measurements by Kawarazaki *et al.*[1] confirmed the existence of the two magnetic-structure types reported by Grier *et al.*[10] which, they argued, were consistent with spatially heterogeneous ordering of moments having values of 1.86 μ_B at $(\frac{1}{2}\frac{1}{2}\ 0)$ and 1.69 μ_B at $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$. At 4 K, however, Kawarazaki *et al.*[1] found only the $(\frac{1}{2}\ \frac{1}{2}\ 0)$ structure type, contrary to Grier *et al.* Unfortunately, the temperature dependences of these structures were not determined.

Here we report specific heat, resistivity, and magnetic susceptibility measurements on $CeRh_2Si_2$ at ambient pressure and discuss their relationship to magnetic properties obtained by neutron diffraction and quasielastic scattering. Our results allow a new interpretation of the magnetic phase transitions.

A polycrystalline sample of nominal stoichiometry $CeRh_2Si_2$ was prepared by arc melting under an argon atmosphere. The sample, wrapped in tantalum foil and sealed in an evacuated quartz tube, was annealed for 10 days at 800 °C. Powder x-ray diffraction at room temperature showed only peaks corresponding to the expected tetragonal $ThCr_2Si_2$ structure (space group $I4/mmm$, number 139). A Rietveld analysis, with the lattice constants as the only free-fit parameters and Si as an internal standard, gave lattice parameters $a=4.088$ Å and $c=10.178$ Å, in agreement with neutron-diffraction studies.[11,10] No secondary phases could be detected in optical or scanning electron microscopy (detection limit $\approx$1% vol). Magnetic susceptibility was determined with a commercial superconducting quantum interference device magnetometer and resistivity data were collected using a low-frequency 4-lead bridge. Specific heat was measured on a 2.549 g sample of $CeRh_2Si_2$ by an adiabatic technique in the temperature range 0.4–45 K. A barely noticeable peak appeared near 5 K in the specific-heat data. We attribute this feature to antiferromagnetic order in second phase $CeRh_3Si_2$, which has a T_N of 5 K.

To confirm this interpretation of the 5 K anomaly, we performed specific heat and resistance measurements on separately prepared $CeRh_3Si_2$. Results of these measurements are shown in Fig. 1(a). A comparison of these results with the small 5 K anomaly found in $CeRh_2Si_2$ implied a concentration of 0.0028 mole $CeRh_3Si_2$ impurity per mole $CeRh_2Si_2$ in our sample. Figure 1(b) shows the x-ray-diffraction pattern of $CeRh_3Si_2$ at room temperature. $CeRh_3Si_2$ crystallizes in the $LaRh_3Si_2$ structure (Ref. 12, *Imma*, 74). We determined the orthorhombic lattice parameters $a=7.128$ Å, $b=9.725$ Å, and $c=5.595$ Å by Rietveld analysis. $CeRh_3Si_2$ and $CeRh_2Si_2$ are two compounds in thermal equilibrium according to the phase diagram by Moroskin

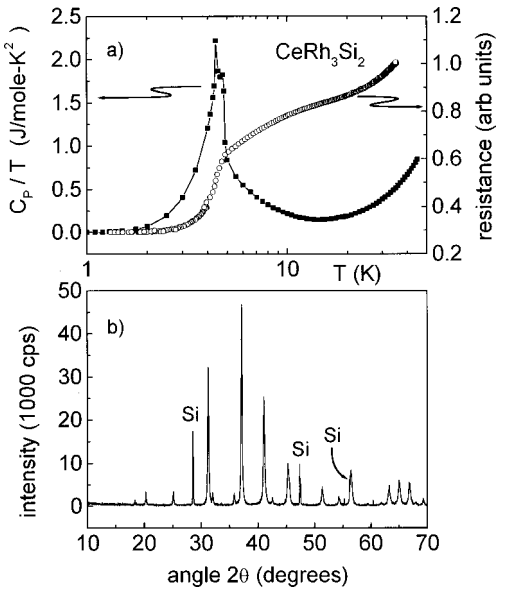

FIG. 1. (a) Specific heat C_p divided by temperature T (left axis) and resistance (right axis) vs the logarithm of temperature for $CeRh_3Si_2$ at zero pressure. (b) X-ray spectrum of $CeRh_3Si_2$. Three peaks of the internal silicon standard are also visible.

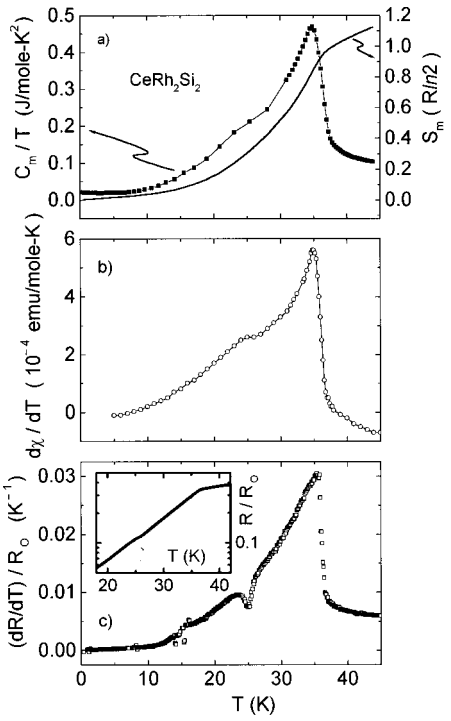

FIG. 2. (a) Magnetic specific heat C_m of $CeRh_2Si_2$ divided by temperature (left axis) as a function of temperature. The solid curve is the magnetic entropy S_m divided by R ln 2 (right axis) as a function of temperature. (b) Temperature-dependent derivative of the magnetic susceptibility $d\chi/dT$ as a function of temperature. (c) Temperature-dependent derivative of the resistance dR/dT vs temperature. The data are normalized to $R_o \equiv R(294\,\mathrm{K})$. (The weak shoulder and data scatter near 15 K are not intrinsic to the sample but arise from an established temperature-control instability that occurs only over a limited temperature interval around 15 K). Inset: Logarithm of normalized resistance vs temperature.

and Seropegin.[13] It is, therefore, not surprising to find $CeRh_3Si_2$ as a minor impurity in $CeRh_2Si_2$ samples. Having prepared a nominally stoichiometric sample and detected such a small amount of impurity suggests that $CeRh_2Si_2$ is an ordered line compound with no homogeneity range. This is not in contradiction with the investigation by Ishikawa and co-workers[14] who found a narrow solid solution of $\approx$1 at. % in the isostructural compound $CeCu_2Si_2$, via the rapid variation of T_c as a function of concentration. The atomic radii of Ce, Rh, and Si are very different and site disorder and a corresponding solid solution seem rather unlikely, in agreement with site occupation refinements by Grier *et al.*[10] and Quezel *et al.*[11] in $CeRh_2Si_2$. No traces of superconductivity at ambient or at high pressure have been found in pure $CeRh_3Si_2$ down to 40 mK. Consequently, this compound does not account for ''dirt effects'' that seem necessary to explain the appearance or absence of superconductivity in $CeRh_2Si_2$ near 9 kbar.[15] Such dirt effects must arise from very subtle differences among samples and equally well could be expected to influence details of the magnetic interactions. These differences have not been detected by conventional metallurgical methods and probably have short-range character. Indications for subtle crystallographic disparities in $CeRh_2Si_2$ are suggested by the rather large R value obtained from neutron-diffraction refinements of the nuclear peaks.[10] There also exist hints for a correlation between residual resistivity and the appearance of superconductivity in $CeRh_2Si_2$.[16]

Specific-heat data on $CeRh_2Si_2$ presented below have been corrected for the contribution from the small amount of second phase $CeRh_3Si_2$. To obtain the magnetic contribution to the specific heat of $CeRh_2Si_2$, we subtracted the specific heat C_L of nonmagnetic $La(Ru_{0.5}Rh_{0.5})_2Si_2$ (Ref. 17) from the total specific heat C_T of $CeRh_2Si_2$, with the assumption that C_L allowed a reasonable estimate of the phonon contribution to C_T at high temperature, i.e., the magnetic specific heat $C_m = C_T - C_L$. The low-temperature behavior of $La(Ru_{0.5}Rh_{0.5})_2Si_2$ is that of a normal metal with a rather large, intrinsic $\gamma = 6$ mJ/mole K^2.[17]

Figure 2(a) shows C_m divided by temperature T for $CeRh_2Si_2$. Also plotted are the temperature-dependent derivatives of the magnetic susceptibility ($d\chi/dT$) and resistance (dR/dT) [Figs. 2(b) and 2(c)]. The sharp anomaly in all three curves near $T_N = 35$ K signals the onset of magnetic order. The solid line in Fig. 2(a) is the integral $\int_0^T C_m(\tau)/\tau d\tau$ and gives the magnetic entropy S in units of R ln 2 as a function of temperature. $S(T)$ reaches the value R ln 2 at a temperature just above T_N. This clearly rules out ordering of free-ion moments since this would generate magnetic entropy of R ln 6 = 14.9 J/mole K. Further, neutron scattering on isostructural CeM_2Si_2 compounds finds[18] that the splitting between the Γ_7 crystal-field groundstate doublet and the first excited state ranges from about 100 to over 200 K, temperatures much larger than T_N in $CeRh_2Si_2$, consistent with a recent estimate[19] of 300 K for this splitting in $CeRh_2Si_2$. The curves C_m/T and $d\chi/dT$ in Fig. 2 exhibit a second, much weaker feature near 24 K. This is not an artifact of the phonon subtraction as similar behavior is found in C_T/T. A weak shoulder above 20 K can also be distinguished in $C_m(T)$ in Fig. 1 of Ref. 17. The feature near 24 K is clearly visible in dR/dT vs T [Fig. 2(c)], but can already be detected

in the resistance curve [inset of Fig. 2(c)].

In view of the various neutron-diffraction results and our measurements, we suggest the following interpretation: Magnetic ordering occurs initially below T_N in the $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ structure with an ordered moment ($1.69\ \mu_B$) less than expected for a Γ_7 crystal-field ground state. The reduced moment is consistent with partial Kondo-like spin compensation of the Ce^{3+} moment, as suggested from quasielastic neutron scattering on $CeRh_2Si_2$, which gives a spin-fluctuation temperature $T_K = 33$ K at $T \geqslant T_N$.[20] The quasielastic linewidth $\Gamma/2 = T_K$ decreases approximately linearly with decreasing temperature and extrapolates to zero near 25 K. Near the temperature where $\Gamma/2 \rightarrow 0$, regions of the sample begin to order in the $(\frac{1}{2}\ \frac{1}{2}\ 0)$ structure with larger moment ($1.86\ \mu_B$), which is favored by the substantially suppressed spin fluctuations. Regions of $(\frac{1}{2}\ \frac{1}{2}\ 0)$ structure grow with decreasing temperature at the expense of $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ domains. The heterogeneous nature of this ordering arises from small spatial variations in the exchange parameter J, the magnitude of which depends very sensitively on details of the local environment around each Ce ion. Such subtle crystallographic effects may also account for the occasional appearance of superconductivity in $CeRh_2Si_2$ at pressures near and above 9 kbar.[7] In the absence of heterogeneity, we speculate that this magnetic-magnetic transition near 24 K should be first order. Indeed, strain measurements on a single crystal of $CeRh_2Si_2$ show a c-axis anomaly that is consistent with a first-order transition near 26 K.[19] We also note that the resistive feature for this phase transition appears to depend strongly on pressure.[21] Such behavior could be understood from the Clausius-Claperon relation if the latent heat associated with a first-order transition were very small.

Inspection of Fig. 2(a) shows clearly that most of the magnetic entropy is associated with ordering of the $4f$ moments at the upper transition. This transition at 35 K shows behavior typical of a second-order phase transition in specific heat, susceptibility and resistance (no hysteresis) measurements. As indicated above, the situation is less clear for the anomaly near 24 K. According to our interpretation, the 24 K transition marks the appearance of a two-phase mixture of the magnetic order parameter. If this first-order transition were spatially smeared by subtle inhomogeneity, as our data suggest, we would not expect a jump in C_m/T, i.e., a discontinuity of the temperature-dependent derivative of the magnetic entropy. However, for a crystallographically perfect sample, a small latent heat should be observed. More detailed temperature-dependent specific-heat data on high quality samples are required to address this issue.

A second-order antiferromagnetic transition (T_{NH}) followed at lower temperatures by a first-order moment-reorientation transition (T_{NL}) has been reported recently[22] in isostructural $Ce(Cu_{1-x}Ni_x)_2Ge_2$ for $x = 0.02$. For $x = 0$, only weak anomalies in thermal expansion and specific heat appear at T_{NL}. Therefore, in contrast to $CeRh_2Si_2$, it seems that in this system[22] a very small amount of disorder is required to induce a first-order transition. Interestingly, the ratio $T_{NH}/T_{NL} \approx 1.67$ in $Ce(Cu_{1-x}Ni_x)_2Ge_2$ is similar to the ratio of magnetic transition temperatures in $CeRh_2Si_2$.

In summary, we have distinguished two magnetic phase transitions in $CeRh_2Si_2$ at 35 and 24 K by specific heat, susceptibility, and resistance measurements. We attribute the high temperature transition to magnetic ordering that occurs below 35 K in the $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ structure with an ordered moment of $1.69\ \mu_B$. Below 24 K, phase separation sets in. Domains of the $(\frac{1}{2}\ \frac{1}{2}\ 0)$ structure with a magnetic moment of $1.86\mu_B$ grow at the expense of the $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ structure without disrupting the evolution of the overall magnetic order parameter. The small entropy associated with the transition near 24 K suggests that the free-energy difference between these two magnetic states also is very small; therefore, the balance between them is susceptible to very minor perturbations and could be expected to be strongly sample dependent. An interesting possibility is that the ''inhomogeneity'' is to a large extent intrinsic to the microscopic competition among electronic, magnetic, and structural degrees-of-freedom in $CeRh_2Si_2$. The interpretation provided by our data reconciles conflicting observations of neutron-diffraction measurements.[1,10,11] In addition, the orthorhombic compound $CeRh_3Si_2$ was discerned as a possible and likely magnetic impurity in $CeRh_2Si_2$ samples. $CeRh_3Si_2$ orders near 5 K at ambient pressure and does not show signs of superconductivity to 40 mK and at pressures to 15 kbar.

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[1] S. Kawarazaki, Y. Kobashi, J. A. Fernandez-Baca, S. Murayama, Y. Onuki, and Y. Miyako, Physica B **206-207**, 298 (1995).

[2] M. J. Besnus, J. P. Kappler P. Lehmann, and A. Meyer, Solid State Commun. **55**, 779 (1985).

[3] J. D. Thompson, J. O. Willis, C. Godart, D. E. MacLaughlin, and L. C. Gupta, Solid State Commun. **56**, 169 (1985).

[4] P. Haen, J. Flouquet, F. Lapierre, P. Lejay, and G. Remenyi, J. Low Temp. Phys. **67**, 391 (1987).

[5] C. Sekine, Y. Nakazawa, K. Kanoda, T. Sakakibara, S. Murayama, I. Shirotani, and Y. Onuki, Physica B **230-232**, 172 (1997).

[6] T. Taniguchi, Y. Tabata, H. Tanabe, and Y. Miyako, Physica B **230-232**, 123 (1997).

[7] R. Movshovich, T. Graf, D. Mandrus, J. D. Thompson, J. L. Smith, and Z. Fisk, Phys. Rev. B **53**, 8241 (1996).

[8] S. Doniach, in *Valence Instabilities and Related Narrow Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977), p. 169.

[9] T. Graf, J. D. Thompson, M. F. Hundley, R. Movshovich, Z. Fisk, D. Mandrus, R. A. Fisher, and N. E. Phillips, Phys. Rev. Lett. **78**, 3769 (1997).

[10] B. H. Grier, J. M. Lawrence, V. Murgai, and R. D. Parks, Phys. Rev. B **29**, 2664 (1984).

[11] S. Quezel, J. Rossat-Mignod, B. Chevalier, P. Lejay, and J. Etourneau, Solid State Commun. **49**, 685 (1983).

[12] K. Cenzual, B. Chabot, and E. Parthé, Acta Crystallogr., Sect. C:

Cryst. Struct. Commun. **44**, 221 (1988).
[13] A. V. Morozkin and Yu. D. Seropegin, J. Alloys Compd. **237**, 124 (1996).
[14] M. Ishikawa, H. F. Braun, and J.-L. Jorda, Phys. Rev. B **27**, 3092 (1983).
[15] J. D. Thompson, Physica B **223&224**, 643 (1996).
[16] J. D. Thompson *et al.* (unpublished).
[17] R. Calemczuk, E. Bonjour, J. Rossat-Mignod, and B. Chevalier, J. Magn. Magn. Mater. **90&91**, 477 (1990); R. Calemczuk (private communication).
[18] A. Severing, E. Holland-Moritz, B. D. Rainford, S. R. Culverhouse, and B. Frick, Phys. Rev. B **39**, 2557 (1989).
[19] R. Settai, A. Misawa, S. Araki, M. Kosaki, K. Sugiyama, T. Takeuchi, K. Kindo, Y. Haga, E. Yamamoto, and Y. Onuki, J. Phys. Soc. Jpn. **66**, 2260 (1997).
[20] A. Severing, E. Holland-Moritz, and B. Frick, Phys. Rev. B **39**, 4164 (1989).
[21] F. M. Grosche, S. R. Julian, N. D. Mathur, F. V. Carter, and G. G. Lonzarich, Physica B **237-238**, 197 (1997).
[22] G. Sparn, M. Deepe, L. Donnevert, C. Geibel, P. Hellmann, K. Heuser, M. Köppen, M. Lang, F. Laube, A. Link, S. Thomas, and F. Steglich, Physica B **230-232**, 317 (1997).