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Competing ground states in heavy-fermion materials

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Abstract

Competing interactions in the presence of coupled spin, charge, and lattice degrees of freedom in heavy-fermion materials lead to a near degeneracy of ground states in some systems. A small perturbation in unit-cell volume or composition subsequently can produce a qualitative change in the ground state, for example, from magnetically ordered to superconducting, with, in some instances, the appearance of a non-Fermi-liquid (NFL) state near their boundary. We have studied two heavy-fermion materials, $CeCu_2Si_2$ and $CeRh_2Si_2$, which illustrate these behaviors. Measurements of the atomic structure of $CeCu_{2+x}Si_2$ as a function of x suggest that structural inhomogeneity may influence the preferred ground state and the existence of NFL behavior in this material. Thermal expansion measurements on $CeRh_2Si_2$ as a function of pressure reveal the evolution of spin-lattice coupling as the balance between RKKY and Kondo interactions is tuned by small volume changes.

Keywords: Pressure; Thermal expansion; Heavy fermions; Kondo effects; Neutron diffraction; Phase transitions

1. Introduction

Exact solution of the single-impurity Kondo problem [1] represented a significant achievement of many-body theory. However, the heavy-fermion problem, requiring the solution of a periodic array of approximately 10^{23} interacting 'Kondo-impurities,' remains a challenge. Experiments show that heavy-fermion systems act as a collection of non-interacting Kondo impurities at sufficiently high temperatures, but at much lower temperatures, their description in terms of electronic band structure is usually more appropriate. De Haas–van Alphen studies reveal quasiparticle masses 10–100-times the bare electron mass, consistent with a very large Sommerfeld coefficient of specific heat [2]. That is, the ground state should be considered to be a strongly renormalized Landau Fermi liquid. Intermediate to the high and low temperature limits, it is reasonable to expect a Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction among the partially spin-compensated Kondo impurities. How the balance between these competing interactions evolves as a function of decreasing temperature determines, in part, whether the ground state is paramagnetic or ordered magnetically.

In the absence of a microscopic theory of heavy-fermion materials, experiment has been guided partially by an intuitively appealing model that considers a one-dimensional necklace of Kondo impurities with RKKY interactions [3]. Both Kondo and RKKY interactions depend on the product $|J|N(0) = g$, where $|J|$ is the magnitude of the magnetic exchange and $N(0)$ is the electronic density of states at the Fermi energy; the former interaction increases exponentially with g and the latter as g^2. As a function of increasing g, this model predicts that the Néel temperature T_N initially increases, passes over a maximum and then decreases to zero at a critical value of the coupling constant g_c. From pressure studies of Kondo-impurity systems, Schilling [4] has shown that $|J|$ is strongly volume dependent, and, indeed, experiments [5] on Kondo-lattice materials as a function of pressure qualitatively follow the predicted variation of $T_N(g)$.

Recently, attention has focused on heavy-fermion materials in which g_c has been approached by application of pressure and/or by chemical alloying [6]. As the Néel temperature is driven to zero temperature at g_c, i.e. toward a zero-temperature phase transition called a quantum-critical point, fluctuations in the antiferromagnetic correlations are expected to slow down and grow spatially. The existence of such long-lived, spatially extended fluctuations would invalidate Landau's Fermi-liquid picture. Interestingly, in some materials, e.g. isostructural $CePd_2Si_2$, $CeCu_2Si_2$ and $CeNi_2Ge_2$, superconductivity appears near g_c and may develop out of a non-Fermi-Liquid (NFL) state [7,8]. When g_c is approached by chemical alloying, as in $CeCu_{6-x}Au_x$, clear deviations

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from Fermi-liquid behavior are evident in thermodynamic properties [9] as well as in the spin dynamics [10,11], but superconductivity has never been observed in these cases. Several theoretical models have been proposed that would lead to a NFL ground state. For purposes here, these models fall into two categories, those that explicitly include effects of disorder [12–14] and those that do not [15–18]. The relative merit and applicability of these two classes of models are currently topics of debate.

For heavy-fermion materials poised near g_c, small perturbations in sample volume or chemical composition produce a qualitative change in the ground state, i.e. at least two nearly degenerate ground states are easily sampled by very small changes in a control parameter. Here we consider two such materials $CeCu_2Si_2$ and $CeRh_2Si_2$, which may be either antiferromagnetic or superconducting depending on applied pressure or in the case of $CeCu_2Si_2$ on Cu stoichiometry at atmospheric pressure.

2. Experimental details

$CeRh_2Si_2$, $CeCu_{1.9}Si_2$ and $CeCu_{2.3}Si_2$ were prepared by conventional arc melting. Powder X-ray diffraction showed that $CeRh_2Si_2$ and $CeCu_{1.9}Si_2$ were single phase in the $I4/mmm$ space group symmetry. Rietveld refinement of neutron powder-diffraction data confirmed the average or global structure type and phase purity of $CeCu_{1.9}Si_2$. Similar measurements on $CeCu_{2.3}Si_2$ indicated a two phase mixture of $CeCu_2Si_2$ and Cu that accounted well for the nominal stoichiometry. Magnetic susceptibility and specific heat measurements on $CeRh_2Si_2$ at ambient pressure found antiferromagnetic ordering at 35 K and a second magnetic transition at 24 K, in agreement with previous reports [19]. Resistance and specific heat C measurements on $CeCu_{1.9}Si_2$ showed an incomplete resistive transition to a superconducting state beginning at ~0.7 K and a weak shoulder in specific heat near the same temperature. Together these imply that superconductivity developed in only a small fraction of the sample and was not representative of the bulk. In contrast, ac magnetic susceptibility measurements on $CeCu_{2.3}Si_2$ found a large, sharp anomaly at 0.7 K, consistent with bulk superconductivity and previous reports [20,21] that excess Cu was necessary to induce bulk superconductivity at ambient pressure.

The local atomic structures of $CeCu_{1.9}Si_2$ and $CeCu_{2.3}Si_2$, reported below, were determined by pair distribution function (pdf) analysis of neutron powder-diffraction data. Data were obtained in the temperature range 10–300 K at the Argonne National Laboratory Intense Pulsed Neutron Source using the glass, liquid, amorphous materials diffractometer (GLAD). These data were corrected for absorption and incoherent scattering as well as for multiple and inelastic scattering to obtain the structure function $S(Q)$, where Q is the momentum transfer, for Q out to $Q = 33$ Å^{-1}. The pdf, calculated by Fourier transforming the $S(Q)$, is a real-space representation of atomic pair correlations [22].

The linear thermal expansion $\Delta l_s/l_s$ of $CeRh_2Si_2$ was measured as a function of pressure to 18 kbar and over the temperature range 8–100 K. The temperature- and pressure-dependent change in sample length Δl_s and the change in length of the reference material copper Δl_{Cu} were detected using a strain-gauge method in a half-bridge circuit to perform the subtraction $\Delta l_s/l_s - \Delta l_{Cu}/l_{Cu}$ electrically. The linear coefficient of thermal expansion α of $CeRh_2Si_2$ was calculated from the temperature derivative of $(\Delta l_s/l_s - \Delta l_{Cu}/l_{Cu})$ and the literature value for the thermal expansion coefficient of Cu [23]. Quantitative measurements of α were only possible above ~8 K because of self-heating of the two 120-Ω strain gauges, which dissipated approximately 4 mW of power in the pressure cell. From measurements of the anisotropic magnetic susceptibility of the $CeRh_2Si_2$ sample, we deduced that the polycrystalline sample exhibited preferential grain orientation and that α was dominated by the c-axis. Hydrostatic conditions in the pressure cell were provided by a Fluorinert pressure medium, and the pressure in the cell was determined from shifts in the inductively-measured superconducting transition temperature of Pb.

3. Results and discussion

3.1. $CeCu_2Si_2$

Detailed studies [24] of $CeCu_{2+x}Si_2$ have established that the ground state is extremely sensitive to x. For slight Cu deficiency ($x<0$), the material exhibits some form of weak magnetism below 0.6–0.8 K, and with a slight excess of Cu ($x>0$), magnetism is replaced with bulk, heavy-fermion superconductivity at $T_c = 0.65$ K. Samples having $|x| \approx 0$ exhibit properties consistent with the coexistence of weak magnetism and superconductivity. Application of a magnetic field of ~4 T, sufficient to suppress superconductivity completely, permits investigation of the temperature variation of resistivity and specific heat to very low temperatures. These studies have shown that, under these conditions, the low-temperature resistivity $\rho \propto T^{3/2}$ and $C/T = \gamma - AT^{1/2}$, which contrast with $\rho \propto T^2$ and $C/T = \gamma$ that are characteristic of a Landau Fermi liquid. On the other hand, samples that are weakly magnetic show $\rho \propto T^2$ and a NFL variation of C/T. Applying a few kilobars of hydrostatic pressure to these samples suppresses evidence for magnetism and bulk superconductivity develops below $T_c \sim 0.6$ K. The very complex behaviors found in $CeCu_{2+x}Si_2$ suggest that it is situated delicately near a quantum-critical point, i.e. very near g_c [7,8]. The absence of any detectable variation in lattice parameters and structure type, by X-ray diffraction,

among these various samples has led to an interpretation [7,8] of the NFL behavior in terms of models that explicitly exclude effects of disorder.

There is now ample evidence [25] for local structural inhomogeneity in correlated electron materials in which there is strong coupling among spin, charge and lattice degrees-of-freedom. In many cases, this inhomogeneity has been revealed through pair distribution function analysis of neutron-diffraction data. However, pdf, to our knowledge, has never been applied to a heavy-fermion material.

Fig. 1a shows the pdf of $CeCu_{1.9}Si_2$ at 10 K. A maximum in the pdf corresponds to the probability of finding a pair of atoms separated by a distance R, and the area under a maximum gives the total number of atoms at this distance. The solid line is the expected pdf, calculated from a model for the average (or global) crystal structure determined by conventional Rietveld refinement based on the $I4/mmm$ symmetry. Using the atomic coordinates and unit-cell dimensions, the model pdf is constructed assuming no local disorder. Good agreement between the calculated and measured pdf implies that the crystallographic structure on the scale of a few unit cells is the same as the structure averaged over the entire sample volume. On the other hand, a rather different conclusion must be reached from the data shown in Fig. 1b for superconducting $CeCu_{2.3}Si_2$. In this case, the local structure is not well represented by the calculated model that also is based on Rietveld refinement of the average crystal structure, including elemental Cu as a second phase. Comparison of the calculated structures in Fig. 1a and b shows that the global structures of $CeCu_{1.9}Si_2$ and $CeCu_{2.3}Si_2$ are essentially identical, as concluded [26,27] from earlier X-ray and neutron-diffraction studies on $CeCu_{2+x}Si_2$. However, inspection of the pdf in Fig. 1b indicates significant discrepancies between local and average crystal structures. The presence of a shoulder at 2.6–2.7 Å, off a main peak at 2.5 Å, suggests a variation in the Ce/Cu–Si pair correlations. Likewise, the difference between measured and calculated peak heights at 3.2, 3.6 and 4.5 Å serve as strong indications for local structural disorder. Although we have not yet developed a model that accurately reproduces the measured pdf, it is clear from Fig. 1b that the structure of $CeCu_{2.3}Si_2$ is not homogeneous.

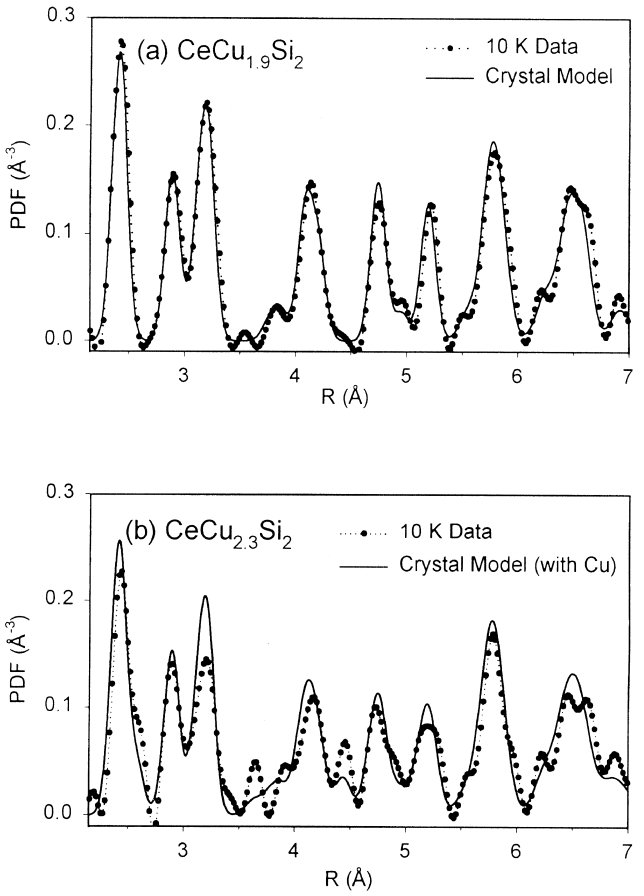

Fig. 1. (a) Pair distribution function (pdf) as a function of radial distance R, determined on non-superconducting $CeCu_{1.9}Si_2$ at 10 K. The solid curve through the data (symbols) was calculated on the basis of Rietveld refinement of the average structure of the sample volume. (b) Measured pdf (symbols) and calculated pdf (solid curve), as in (a), for the bulk superconductor $CeCu_{2.3}Si_2$ at 10 K.

3.2. $CeRh_2Si_2$

The metallurgy of $CeRh_2Si_2$ has been studied in much less detail than $CeCu_2Si_2$, and it is not known to what extent its properties may depend on precise stoichiometry. Like $CeCu_2Si_2$, the magnetic state in $CeRh_2Si_2$, can be suppressed by modest pressures, $P_c = 10 \pm 1$ kbar, and in some samples, superconductivity appears below ~400 mK as the magnetic–non-magnetic boundary is approached with pressure [28]. Perhaps coincidentally, superconductivity in $CeCu_2Si_2$ and $CeRh_2Si_2$ occurs when their unit-cell volumes are equal [29]. Low-temperature specific heat and resistivity measurements [30] as a function of pressure above and below P_c show Fermi-liquid temperature dependences, even when resistivity measurements were made [19] close to P_c. The absence of NFL behavior and the very strong pressure dependence of T_N near P_c ($\partial T_N/\partial P \approx -20$ K kbar^{-1}) have led to the suggestion [19] that the transition may become weakly first order.

To explore the thermodynamics of $CeRh_2Si_2$ over a broader temperature range and in finer pressure increments than used in specific heat studies, we have measured its linear thermal-expansion coefficient α as explained in Section 2. Because of limitations in the technique, it has not been possible to determine α quantitatively near P_c and at temperatures well below 10 K where NFL effects might be most pronounced. Representative data shown in Fig. 2a clearly indicate strong coupling between spin and lattice degrees-of-freedom. Two well-defined anomalies at $P = 1$ bar signal the onset of antiferromagnetism at 35 K and a spin rearrangement at 24 K. The large, negative-going features in α at these transitions, combined with specific heat measurements and Ehrenfest's relationship,

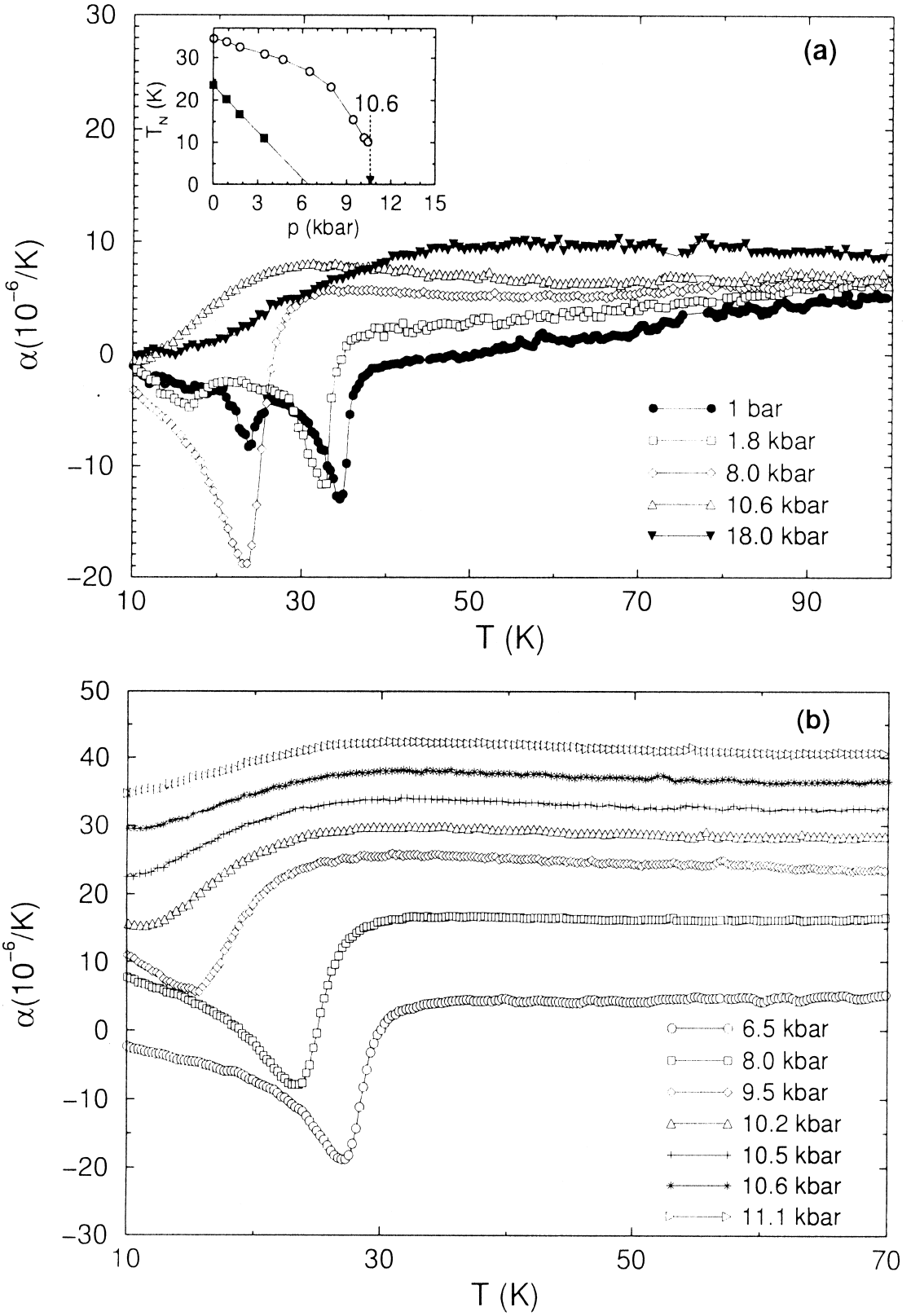

Fig. 2. (a) Linear thermal expansion coefficient versus temperature for $CeRh_2Si_2$ at representative pressures. The inset shows the pressure dependence of magnetic transitions in $CeRh_2Si_2$ obtained from $\alpha(T,P)$. (b) Evolution of the linear thermal expansion coefficient of $CeRh_2Si_2$ as a function of pressure. For clarity, curves have been displaced vertically by arbitrary values.

imply that these transitions should decrease rapidly with pressure, which agrees with the phase diagram shown in the inset of Fig. 2a.

Thermodynamics of a Fermi liquid requires that $\alpha(T)$ approach zero as $T \rightarrow 0$. Focussing on the 1-bar data in Fig. 2a, we see that sharp anomalies in $\alpha(T)$, signaling magnetic transitions, emerge from a 'background' in which $\alpha(T)$ is negative and is passing through a broad minimum before reaching zero at $T = 0$. Data at 10.6 kbar and higher show no evidence for a phase transition and a broad maximum in $\alpha(T)$ centered at a temperature T_m that increases at a rate of 2–3 K kbar^{-1}. The evolution of qualitative changes in the shape of $\alpha(T)$ at intermediate pressures is apparent in Fig. 2b. As P_c is approached from $P < P_c$, the anomaly associated with T_N becomes progressively less obvious, eventually becoming a shallow minimum that moves to lower temperatures as the maximum in $\alpha(T)$ at higher temperatures becomes more pronounced. Though a negative thermal expansion and a minimum in $\alpha(T)$ at low temperatures might arise from lattice anharmonicity [31], the strong pressure dependence of the minimum and its existence only in the presence of Néel order argues that it comes primarily from the competition between RKKY and Kondo interactions in $CeRh_2Si_2$.

Thermodynamically, the volume–thermal expansion coefficient $\beta(T)$ and specific heat are proportional. Assuming the temperature dependence of $\alpha(T)$ reflects that of $\beta(T)$ and that the maximum in $\alpha(T)$ comes from a Kondo-impurity-like effect [32], then the shape of $\alpha(T)$ should be described by a Kondo-impurity model for the specific heat. Using the Schotte and Schotte model [33] for the specific heat of a spin-1/2 Kondo impurity, we find that this model well-reproduces the shape of $\alpha(T)$, especially near P_c, but only if we assume the density of states is centered roughly 1 meV above the Fermi energy (Such a shift in the density of states, if it reflects a true physical effect, might influence the presence or absence of NFL behavior close to g_c). Kondo temperatures derived from this model are 25 and 40 K for pressures of 10.6 and 18 kbar, respectively, consistent with a direct measurement [34] of $T_K \approx 35$ K at atmospheric pressure by inelastic neutron scattering. The shift in the maximum in $\alpha(T)$ to higher temperatures with increasing pressure implies $\partial T_K / \partial P > 0$, which is the case in Ce-based heavy-fermion materials [5].

4. Summary

$CeCu_{2+x}Si_2$ and $CeRh_2Si_2$ provide instructive examples where the interplay among degrees-of-freedom and competing interactions leads to near degeneracy of magnetic and superconducting ground states. It appears that bulk superconductivity in $CeCu_{2+x}Si_2$ develops in the presence of local crystallographic inhomogeneity, which also may be a non-negligible factor in producing NFL behavior. An analogy with the high-T_c cuprates is striking: introduction of an additional charge degree-of-freedom (doped holes) produces a cross-over from magnetically ordered to superconducting ground states, structural inhomogeneity in the superconducting state, and unconventional temperature dependences of physical properties. Precisely what role excess Cu in $CeCu_{2+x}Si_2$ plays in producing structural inhomogeneity remains to be explored, as does a direct link between inhomogeneity and superconductivity.

Thermal expansion measurements on $CeRh_2Si_2$ as a function of pressure reveal strong coupling between spin and the lattice and the evolution of this coupling as the balance between RKKY and Kondo interactions is tuned by small changes in cell volume. We find no evidence for a change in the order of the transition from second to first or weakly first order as a function of pressure. Instead, the magnetic signature in $\alpha(T)$ evolves continuously as $P \rightarrow P_c$. Consequently, we might expect to find evidence for quantum-critical fluctuations for $P \approx P_c$ at lower temperatures than accessed in our experiments.

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