Logarithmic Fermi-Liquid Breakdown in $NbFe_2$

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The *d*-electron low temperature magnet $NbFe_2$ is poised near the threshold of magnetism at ambient pressure, and can be tuned across the associated quantum critical point by adjusting the precise stoichiometry within the $Nb_{1-y}Fe_{2+y}$ homogeneity range. In a nearly critical single crystal ($y = -0.01$), we observe a $T^{3/2}$ power-law dependence of the resistivity ρ on temperature T and a logarithmic temperature dependence of the Sommerfeld coefficient $\gamma = C/T$ of the specific heat capacity C over nearly 2 orders of magnitude in temperature, extending down to 0.1 K.

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The standard model of metals, Fermi liquid theory, is expected to break down in clean systems at quantum phase transitions associated with the low temperature border of magnetism [1]. A wide range of possibilities exists, however, regarding the precise nature of this breakdown and of the resulting non-Fermi liquid states. Among these, arguably the mildest form of Fermi-liquid breakdown involves a logarithmic energy dependence of the real part of the quasiparticle self-energy, while the imaginary part becomes linear in energy. In this *logarithmic breakdown* [2], the quasiparticle relaxation rate becomes comparable to the quasiparticle energy all the way down to the Fermi level, so that the quasiparticle resonance marginally cannot be resolved even in the low-energy limit. More drastic forms of Fermi-liquid breakdown are suggested for those materials on which most of the available evidence for Fermi-liquid breakdown near magnetic quantum phase transitions has been collected: in Ce- or Yb-based *f*-electron metals. In some of these, anomalous temperature dependences of the resistivity and of the heat capacity over extended ranges in temperature, as well as Hall coefficient discontinuities [3–6], have been taken to suggest non-Fermi liquid states in which local moments survive down to very low temperatures. These more extreme scenarios contrast with the "conventional" approach, in which the effects of quantum critical magnetic fluctuations are computed within a band picture of magnetism [7]. Clear-cut experimental evidence for the conventional breakdown scenario, paradoxically still scarce, may be found among the *d*-electron systems, because for many of these a band picture is much more clearly appropriate than for the more complex *f*-electron compounds. In particular, the logarithmic Fermi-liquid breakdown scenario has long been expected to be realized at the quantum critical point (QCP) of 3D band ferromagnets (FM). The experimental signature of logarithmic Fermi-liquid breakdown in such systems is a leading-order logarithmic temperature dependence in C/T and a subleading order $T^{5/3}$ contribution to the electrical resistivity [1,7]. More detailed calculations (e.g., [8,9]) suggest that the FM QCP may be inherently unstable, either towards first order transitions or towards long-wavelength modulated structures. Even in these comparatively simple systems a range of phenomena may therefore be expected near the threshold of magnetism.

A number of magnetic transition-metal compounds have been investigated in the search for logarithmic Fermi-liquid breakdown, including MnSi [10], $ZrZn_2$ [11,12], Ni_3Al [13], and Fe [14]. High pressure has been used in these cases to approach the FM QCP. Non-Fermi liquid forms have indeed been observed in transport properties, such as a distinctive $T^{3/2}$ power-law resistivity in MnSi over 3 orders of magnitude in temperature and, very recently, a striking linear-in-T contribution to the thermal resistivity in ambient pressure $ZrZn_2$ [15]. However, the technical constraints intrinsic to high pressure experiments have so far hindered multiprobe investigations. Alloying offers an alternative approach to the FM QCP [16], but the dopant concentration must be minimal. Otherwise, disorder-induced scattering may smear or completely remove phase transitions, or lead to diffusive transport, and site disorder or inhomogeneity may cause cluster or even spin-glass formation, all of which complicate the theoretical description and obscure the objective of the study.

Balanced on the threshold of magnetism at *ambient* pressure, the hexagonal $C14$ Laves phase compound $NbFe_2$ provides a new perspective to this long-standing problem. Stoichiometric $NbFe_2$ has been reported as a rare example of low-temperature spin-density-wave (SDW) order ($T_N \simeq 10$ K) in a *d*-metal system [17,18]. The SDW state grows out of low-ordered-moment FM order, which can be induced by slight Fe excess (Fig. 1). Slight Nb excess, on the other hand, suppresses the SDW ordering temperature, and a QCP ($T_N \rightarrow 0$) is approached close to $\simeq Nb_{1.015}Fe_{1.985}$. Here, we report the first detailed study of a slightly niobium-rich single crystal of $NbFe_2$, which is very close to a magnetic QCP at ambient pressure. We find that the resistivity follows a $T^{3/2}$ power-law temperature dependence between 0.1 and 10 K and that the heat capacity varies logarithmically with temperature between 0.1

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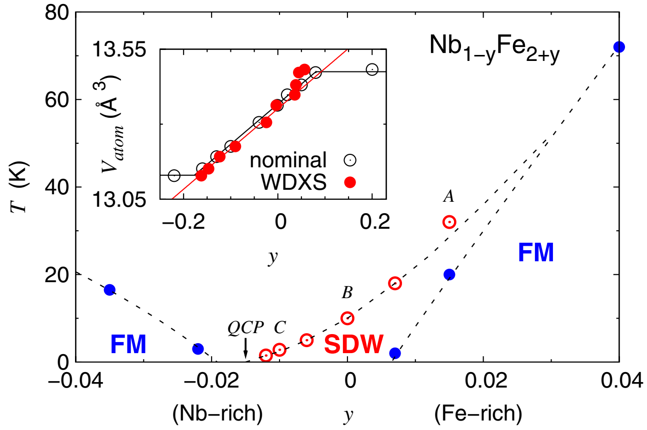

FIG. 1 (color online). By adjusting the precise composition within a narrow homogeneity range, $NbFe_2$ can be tuned from ferromagnetism (FM) ($y > 0.01$) via an intermediate spin-density-wave (SDW) modulated state to a quantum critical point (QCP) ($y \simeq -0.015$). This Letter discusses samples A (Fe-rich, $y = 0.015$), B (stoichiometric), and C (Nb-rich single crystal, $y = -0.01$). The precise composition of these nearly stoichiometric samples has been determined from their unit cell parameters (from powder x-ray diffraction), which were compared against a scale drawn up by measuring the composition of a large number of samples covering the full homogeneity range using wavelength-dispersive x-ray spectroscopy (WDXS) (inset).

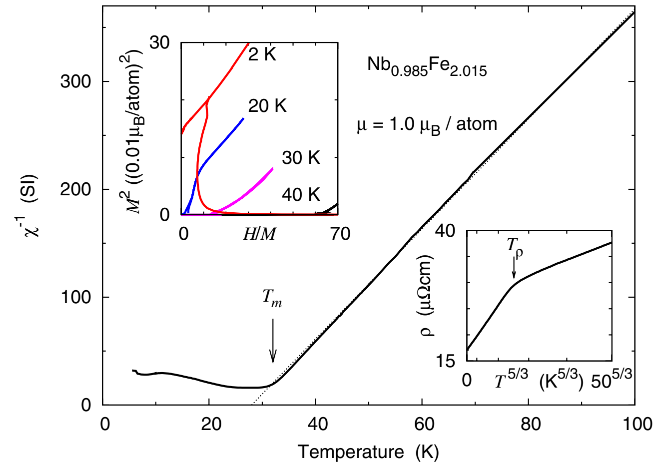

FIG. 2 (color online). Magnetic properties of slightly iron-rich $NbFe_2$ (sample A). The inverse susceptibility follows a Curie-Weiss behavior from 100 K down to $T_m \simeq 32$ K, with fluctuating moment $\simeq 1.0\mu_B/\text{atom}$. Low temperature ferromagnetism is inferred from Arrot plot isotherms (upper left inset), which exhibit typical hysteretic behavior with a remanent magnetization $\simeq 0.04\mu_B/\text{atom}$. The T dependence of the resistivity ρ (lower right inset) exhibits a kink (arrow) just below T_m. Both above and below this kink $\rho(T)$ follows a $T^{5/3}$ power-law form.

and 4 K. These results represent the first demonstration of the key experimental signatures of logarithmic Fermi-liquid breakdown in a pure transition-metal compound.

We present data from an iron-rich polycrystal (sample A, $Nb_{0.985}Fe_{2.015}$), a stoichiometric polycrystal (sample B, $NbFe_2$), and a niobium-rich single crystal (sample C, $Nb_{1.01}Fe_{1.99}$). The polycrystals have been prepared by melting together the elements (99.95% Nb, 4N vacuum-remelted iron) in an argon atmosphere using radio-frequency induction heating on a water-cooled copper boat, immediately followed by a short (1–3 h) anneal near 1000 °C. Similarly, the single crystal has been obtained using a Czochralski method from an induction-heated melt in an argon atmosphere. Measurements of the resistivity, heat capacity, magnetization, and magnetic susceptibility down to 1.8 K have been carried out in a 9 T physical properties measurement system (Quantum Design). High-resolution measurements of the resistivity at temperatures down to 50 mK were obtained in an adiabatic demagnetization refrigerator (Cambridge Magnetic Refrigeration) by a standard 4-terminal ac technique. The low temperature heat capacity was determined in the same refrigerator by a relaxation-time technique.

Slightly Fe-rich $NbFe_2$ represents the point of departure of our investigation (Fig. 2). At 1.5% excess iron, we observe (i) Curie-Weiss behavior in the inverse susceptibility down to $T_m \simeq 32$ K, (ii) a kink in $\rho(T)$ at a slightly lower temperature $T_\rho \simeq 25$ K, and (iii) FM hysteresis loops in the lowest-temperature M-H isotherms. Whereas the low-T state clearly appears ferromagnetic, no ordered moment is observed between T_m and T_ρ. This suggests that the transition at T_m may be into a non-FM ordered state and that the transition to FM order happens only at a lower temperature $T_c \simeq T_\rho < T_m$.

Reducing the Fe excess lowers the magnetic transition temperature and changes the nature of the ordered state. Our findings confirm the reported interpretation that stoichiometric $NbFe_2$ forms a magnetically ordered, but not ferromagnetic, low temperature state (Fig. 3). We note that this state is characterized by a very high magnetic susceptibility $\chi \sim 0.02$, which corresponds to a Stoner enhancement factor $\chi/\chi_0 \simeq 180$, where $\chi_0 \simeq 10^{-4}$ is the bare band structure susceptibility estimated from the calculated density of states $g(E_F) \simeq 40(\text{Ry f.u. spin})^{-1}$ [19]. The enhancement of the specific heat capacity Sommerfeld coefficient $\gamma = C/T \simeq 45$ mJ/mol K^2, with respect to its band structure value $\gamma_0 \simeq 15$ mJ/mol K^2, by contrast, is about 3, leaving a Wilson ratio $R_W = \frac{\chi/\chi_0}{\gamma/\gamma_0} \simeq 60$, which suggests extreme proximity to ferromagnetism. We suspect that the so-far unidentified magnetic order in $NbFe_2$ is a long-wavelength modulated state, possibly helical. The ordering wave vector Q may be estimated as ~ 0.05 Å^{-1}, by inserting the measured $\chi_{q=0} \simeq 0.02$ at T_m into the dispersion $\chi_{\mathbf{q}}^{-1} \simeq c|\mathbf{q} - \mathbf{Q}|^2$ with a typical $c \simeq 2.4 \times 10^4$ Å^2 (value determined for $ZrZn_2$ by neutron scattering). The very small magnetization $M \simeq 0.02\mu_B/\text{atom}$ at just above the critical field leads us to expect, then, a weakly modulated structure with a wavelength of about 130 Å.

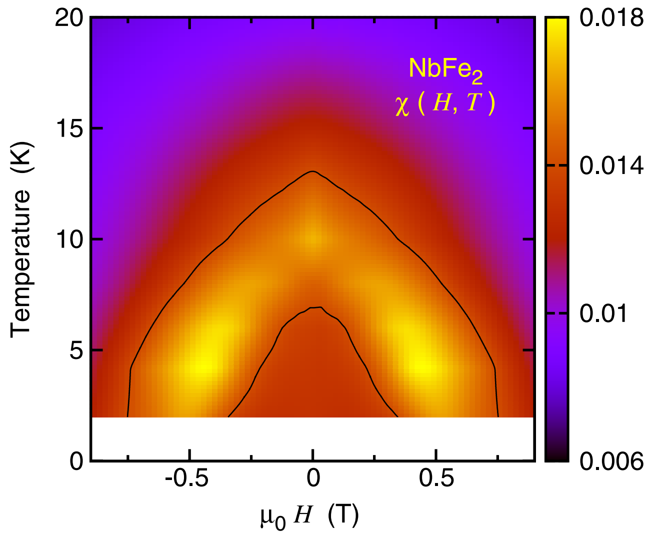

FIG. 3 (color online). Susceptibility map of the low-field, low-temperature sector of the $NbFe_2$ phase diagram (sample B), compiled from isotherms at 2, 4, 6, 8, 10, 12, 15, and 20 K. A line of χ maxima separates the $H = 0$, $T \ll T_m$ state from the high temperature state of $NbFe_2$, suggesting magnetic order at low temperature.

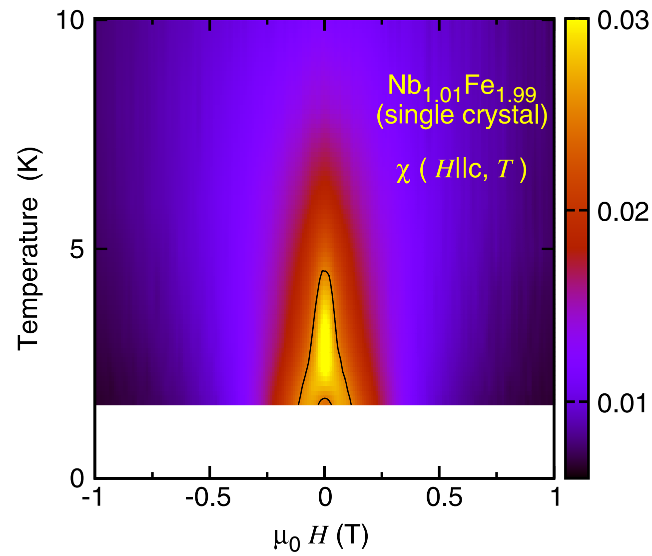

FIG. 4 (color online). Temperature-field map of the magnetic susceptibility ($H \parallel c$) of a nearly quantum critical single crystal (sample C), constructed from χ-H isotherms at 1.6, 2, 2.5, 3, 4, 5, 6, 8, 10, and 12 K. On cooling at zero field, $\chi(H, T)$ builds up into a ridge, which bifurcates into two branches below 2.8 K.

If the iron content in $NbFe_2$ is reduced beyond stoichiometry, our own results as well as literature data [17,18] show that T_m decreases, giving rise to a QCP at a composition close to $Nb_{1.015}Fe_{1.985}$. We have investigated the vicinity of this QCP in a slightly niobium-rich single crystal ($Nb_{1.01}Fe_{1.99}$), which despite its off-stoichiometric composition has the highest residual resistance ratio (RRR $\simeq$ 18) of all the samples presented.

The H-T map of the susceptibility of this single crystal (Fig. 4) suggests magnetic order below $T_m \simeq 2.8$ K and a very small critical field $\mu_0 H_c \simeq 0.2$ T. Transition-metal compounds are governed by band energy scales which are orders of magnitude larger than those of narrow band f-electron compounds. Rescaling temperature by the ratio of the Sommerfeld coefficients brings T_m to a similar *relative* magnitude as, for example, in $YbRh_2Si_2$. Despite its residual, weak low temperature order the resistance of the single crystal follows a $T^{3/2}$ power law down to $T < 0.1$ K, and its heat capacity divided by temperature C/T increases logarithmically without any indication of a crossover to conventional Fermi-liquid behavior (Fig. 5). We have observed qualitatively similar behavior in a number of single crystals of similar composition, but note that the precise value of the resistivity power-law exponent varies between 3/2 and 5/3. By contrast, in stoichiometric samples of $NbFe_2$ ($T_N \simeq 10$ K) $\rho(T)$ recovers a T^2 form below 0.6 K, and C/T saturates for $T < 1$ K (inset of lower panel, Fig. 5) at values far below those observed in the single crystal. The precise form of $\rho(T)$ may depend on stoichiometry and sample orientation. The key result, however, is robust: close to the QCP, both the resistivity and the heat capacity exhibit anomalous temperature dependences consistent with logarithmic Fermi-liquid breakdown.

Our findings raise questions as to (i) why ρ and C/T appear unperturbed by the onset of magnetic order, (ii) the role of disorder, and (iii) the nature of magnetic order in $Nb_{1.01}Fe_{1.99}$. First, the ordered moment below T_m ($< 0.02\mu_B$) represents a tiny fraction of the fluctuating moment: magnetic order is then expected to have only a minor effect on the magnetic fluctuation spectrum and hence on the low-T properties (cf. small C anomaly at $T_N \simeq 10$ K even in stoichiometric sample, inset of Fig. 5). Second, although a $T^{3/2}$ form for $\rho(T)$ has also been observed in spin glasses (e.g., [20]), (i) in spin glasses this form for $\rho(T)$ is only seen below the freezing temperature, whereas here it also holds above T_m, (ii) the dynamic range of the anomalous resistivity is far larger in the pure compounds measured here than in reported spin-glass measurements, and (iii) the measured C/T is completely inconsistent with that found in spin glasses. Finally, while the observed form for $\rho(T)$ cannot decide unambiguously between FM and SDW quantum criticality, the measured C/T is consistent with predictions for a FM QCP. Naively, one would expect only a subleading $\sqrt{T}$ correction to the Fermi-liquid form for the heat capacity close to a SDW QCP, but the situation is less clear, if the SDW ordering wave vector Q is very small. Our bulk measurements as well as theoretical work [8,9] suggest a small wave vector SDW state ($Q \sim 0.05$ Å^{-1}) for stoichiometric $NbFe_2$. Quantitative calculations will be needed to clarify whether a small-Q SDW QCP explains the observed experimental signatures, while renewed neutron studies are

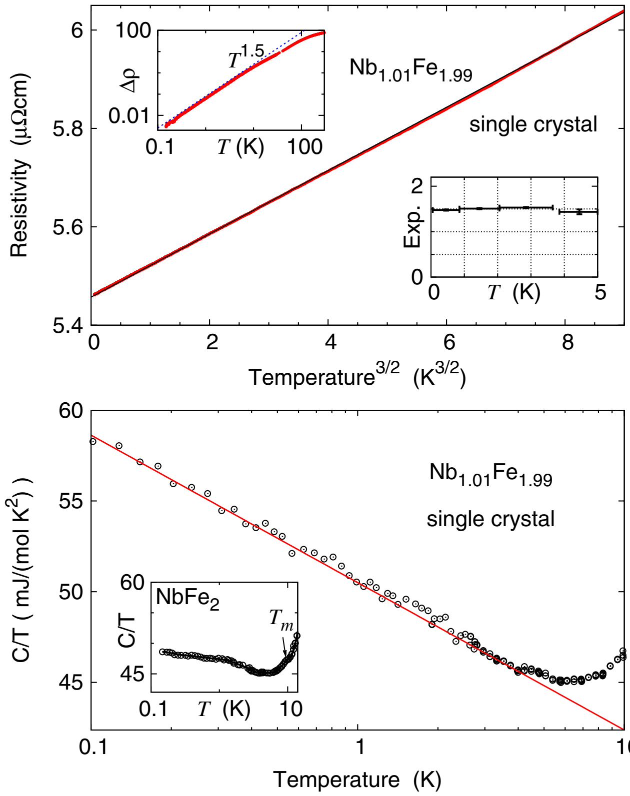

FIG. 5 (color online). Quantum criticality in single crystal $Nb_{1.01}Fe_{1.99}$ (sample C). Upper panel: $\rho(T)$ follows a power-law form with exponent significantly less than the Fermi-liquid value 2 over a wide range in T, down to 0.1 K. A detailed analysis involving piecewise three-parameter fitting of the data (inset, horizontal bars indicate T range; vertical bars indicate precision of exponent estimate) confirms that the power-law exponent locks into a stable value close to $3/2$ over nearly two decades in temperature. Lower panel: The Sommerfeld coefficient C/T displays a distinct logarithmic T dependence, which increases the already high electronic contribution to C/T at 4 K by about 30% on cooling to 0.1 K.

planned to identify the small-moment ordered state of $NbFe_2$.

Among the pure transition-metal compounds—a class of materials believed to be well understood and yet full of surprising twists and discoveries—these findings represent the first clear indication of a logarithmic breakdown of the Fermi liquid state, as expected at a 3D FM QCP. $NbFe_2$ may be sufficiently close to ferromagnetism for its critical behavior to fall into this category. It presents a unique opportunity for multiprobe studies of band-magnet quantum criticality at ambient-pressure.

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