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Correlated f-electron materials near a $T=0$ magnetic–nonmagnetic boundary: implications for δ-Pu

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Abstract

A comparison of magnetic and thermodynamic properties of $CeRh_2Si_2$ and $CeRh_{2-x}Ru_xSi_2$ near their $T=0$ magnetic–nonmagnetic boundary accessed by pressure and alloying, respectively, emphasizes the role of disorder in producing non-Fermi-liquid effects. Spatially varying hybridization induced by crystallographic disorder may play a similar though less dramatic role in determining the physical properties of δ-phase plutonium at ambient and high pressures. © 1998 Elsevier Science S.A.

Keywords: Thermal expansion; Specific heat; $CeRh_{2-x}Ru_xSi_2$; Pu; Gruneisen parameter

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1. Introduction

The ground state of a periodic lattice of Kondo ions, e.g., Ce, U or Pu, is determined by the competition between intersite, Ruderman–Kittel–Kasuya–Yosida (RKKY), interactions and local or intrasite, Kondo, interactions [1]. The balance between these interactions is set by the magnitude of the volume-dependent exchange parameter J which is proportional to V_{kf}^2, the square of the conduction electron–f-electron hybridization matrix element. For small $|J|$, RKKY interactions dominate and the f-moments order magnetically. Whereas, for very strong hybridization, it is energetically favorable for an f-electron to spend a fraction of its time in the conduction band, and in this mixed-valence limit, the ground state is a quantum mechanical admixture of f^n and f^{n-1} configurations. Between these extremes, there should be a crossover from a magnetically ordered state to one with no long range order at some critical J_c.

Tuning V_{kf} by pressure or chemical substitutions allows access to this zero-temperature magnetic–nonmagnetic boundary. Several experiments [2–6] have shown that thermodynamic and transport properties of Ce- and U-based Kondo lattice systems near this boundary are not characteristic of a correlated Fermi liquid but show logarithmic or atypical power-law temperature dependences at low temperatures. Various theoretical models [7–11] have been invoked to account for this non-Fermi-liquid (NFL) behavior but no clear consensus has emerged. However, what is common to many correlated f-electron materials in which NFL effects have been observed is the presence of crystallographic disorder. Such disorder could be expected to produce a statistical distribution in V_{kf} that leads to NFL behavior [5,11]. Indeed, this view accounts well for a wide range of properties in $UCu_{5-x}Pd_x$ [5]. One of the clearer examples for the importance of disorder has come from a comparison of the temperature-dependent specific heat near the magnetic–nonmagnetic boundary in $CeRh_2Si_2$, in which the boundary was accessed by application of pressure, and in $CeRh_{2-x}Ru_xSi_2$, in which the boundary was reached for $x \geq 1$ at ambient pressure [6]. In the former case, there was no evidence for NFL behavior; whereas, in the later, significant NFL behavior could be accounted for by assuming a Gaussian distribution in V_{kf}^2. In the following we show that this same distribution explains a logarithmic divergence of the low-temperature thermal expansion coefficient of $CeRh_{2-x}Ru_xSi_2$ ($x \approx 1$), provided that disorder effects are included in an effective electronic Gruneisen parameter Γ. Similar, though less pronounced, disorder effects may play a role in determining the physical properties of δ-phase plutonium.

2. Experimental details

Polycrystalline samples of $CeRh_{2-x}Ru_xSi_2$, $x=1.0$ and 1.04, were prepared by arc melting in an inert atmosphere. X-Ray powder diffraction confirmed the expected $ThCr_2Si_2$ body-centered tetragonal crystal structure, with

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no detectable second phase. However, specific heat measurements found weak anomalies at 11 and 5 K for $x=1.0$ and 1.04 samples, respectively. The magnetic phase diagram of $\mathrm{CeRh}_{2-x}\mathrm{Ru}_x\mathrm{Si}_2$ [12] suggests that these anomalies are due to the presence of less than one-mole percent of slightly Ru-deficient material. Thermal expansion was measured using a high resolution ($\Delta l/l<10^{-8}$) capacitance dilatometer. Because the sample is polycrystalline, we assume that the volume-thermal expansion coefficient $\beta = 3\alpha_l = 3\,\mathrm{d}\ln l/\mathrm{d}T$, where α_l is the measured linear-thermal expansion coefficient. At most we expect this assumption to introduce a quantitative error in the magnitude of β and not to affect the relevant temperature dependence of β.

3. Results

Fig. 1(a) shows the temperature-dependence of β/T for samples with $x=1.0$ and 1.04. Over an interval spanning approximately one decade in temperature $\beta/T \propto -\ln T$. At these low temperatures, phonons should contribute negligibly and, hence, β is determined predominately by electronic contributions. With this identification, the observed T-dependence of β/T contrasts strongly with $\beta/T=$ const. expected for a Fermi liquid at low temperatures. The logarithmically diverging β/T at low temperatures is similar to behavior found [6] for C_p/T and χ, where C_p is the specific heat and χ is the static magnetic susceptibility. Previous work showed [6] that the T-dependence of C_p/T and χ could be explained with a model in which alloying with Ru produced a distribution of Kondo temperatures through a Gaussian distribution $P(\lambda)$, where $\lambda = |J|N(E_F) \propto V_{kf}^2$ is defined by the relationship $T_K(\lambda) = E_F e^{-1/\lambda}$ and E_F is the Fermi energy. Fits to the data gave a mean value $\lambda_m = 0.175$ and width of the Gaussian $\Delta\lambda = 0.021$.

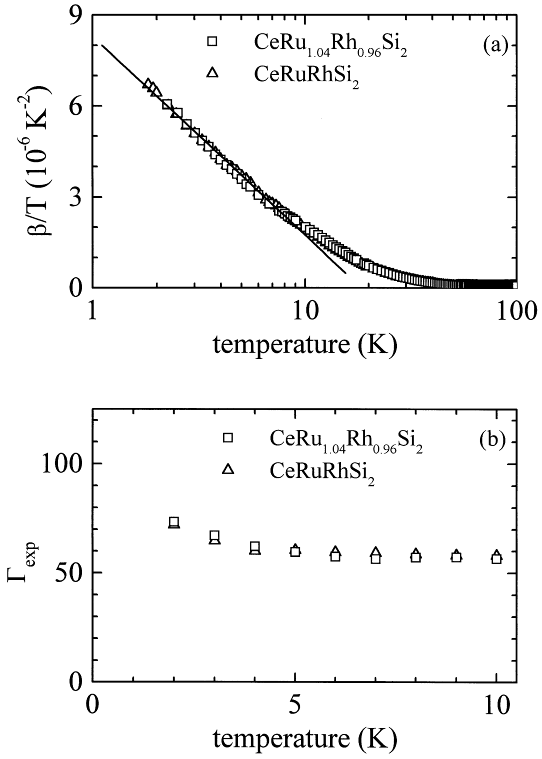

Fig. 1. (a) Volume-thermal expansion coefficient β divided by temperature versus temperature on a logarithmic scale; squares – $x=1.04$, triangles – $x=1.0$. The solid line is a guide to the eye. (b) Experimental Gruneisen parameter obtained from the ratio $(\beta/C_p)(V/\kappa)$; squares – $x=1.04$, triangles – $x=1.0$.

Properties of Kondo-lattice/mixed-valence systems are often analyzed assuming that the electronic contribution to their free energy scales with a characteristic volume-dependent energy scale $T_0(V)$, i.e. $F_e(T,V) = Nk_B Tf(T/T_0(V))$ [13]. T_0 is usually identified as the Kondo or valence-fluctuation temperature. Single energy scaling implies that β is related directly to the specific heat by:

$$\beta/T = \Gamma\kappa C_p/TV, \qquad (1)$$

where κ is the compressibility, V is the volume and Γ is the electronic Gruneisen parameter:

$$\Gamma = -\partial \ln T_0/\partial \ln V. \qquad (2)$$

Eq. (1) shows immediately why the temperature dependence of β/T should resemble that of C_p/T and that local variations in V_{kf}^2 due to crystallographic disorder also should be important for determining β at $T<T_0$, where correlated-electron contributions become significant. By Eq. (1), if Γ and κ are independent of temperature and disorder effects, then $<\beta> = (\Gamma\kappa/V) < C_p>$, where:

$$\langle C_p \rangle = \int_0^\infty P(T_K) C_p^0(T, T_K)\,\mathrm{d}T_K \qquad (3)$$

and $C_p^0(T, T_K)$ is the specific heat in the absence of disorder [5]. That is, the experimental ratio $(<\beta>/<C_p>)(V/\kappa) = \Gamma_{exp}$ should be a constant. However, Fig. 1(b) shows that Γ_{exp} is large and increases with decreasing temperature. Because of the strong volume dependence of T_K implied by the large Γ and of the existence of hybridization disorder, it is more appropriate that:

$$\langle \beta \rangle = \kappa/V \int_0^\infty (-\partial \ln T_K/\partial \ln V) C_p^0(T, T_K) P(T_K)\,\mathrm{d}T_K, \qquad (4)$$

i.e. the product ΓC_p responds to the distribution of Kondo temperatures. Fig. 2 shows Γ_{model} calculated from Eqs. (3) and (4) with $|J| = |J_o|V^{-n}$ and $n=6$ [14]. The distribution $P(T_K)$ used in this calculation was that found earlier from an analysis of C_p and χ in $\mathrm{CeRhRuSi}_2$. We see that including Γ in the integral of Eq. (4) semiquantitatively accounts for the upturn in the measured ratio given in Fig. 1(b).

4. Discussion

Plutonium is a fascinating metal whose physical properties remain poorly understood. Among the various

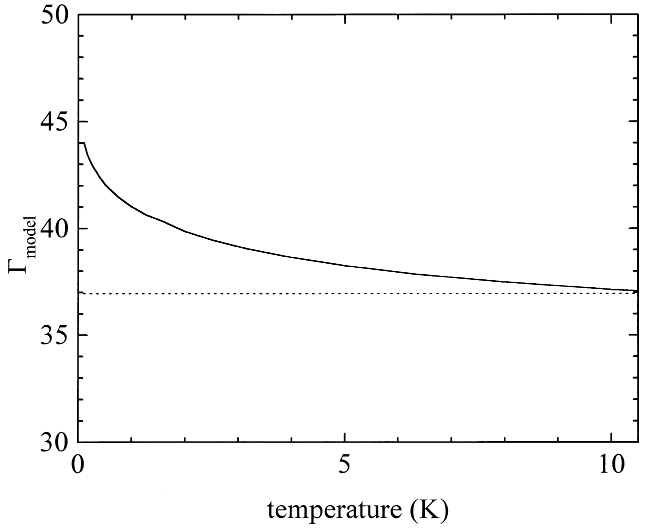

Fig. 2. Calculated Gruneisen parameter as a function of temperature. The dashed line was obtained from Eqs. (1) and (3), i.e. assuming that the distribution of Kondo temperatures does not affect Γ. The solid line was calculated from Eqs. (3) and (4), with κ/V taken as a constant.

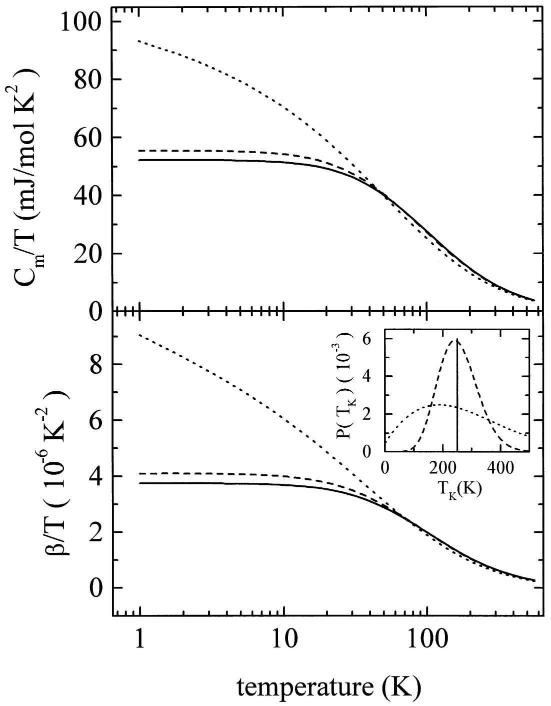

Fig. 3. Temperature dependence of the magnetic specific heat divided by temperature (upper panel) and volume thermal expansion coefficient divided by temperature (lower panel) calculated using Eqs. (3) and (4), respectively. Solid, dashed and dotted curves correspond to distributions of T_K shown in the inset of the lower panel.

structural phases that elemental Pu assumes below its melting point, the fcc δ-phase has the largest cell-volume/atom. At this f–f spacing, δ-Pu is close to a magnetic–nonmagnetic boundary by Hill's criteron [15], and it is generally assumed that the 5f electrons are nearly localized. Substitution of various elements, e.g., Ga, Al, Ce, etc., stabilize the fcc structure to low temperatures where the ground state properties become evident. The electronic specific heat of stabilized δ-Pu is large, ~50 mJ mol^{-1} K^{-2}, characteristic of a correlated electron material [16], and its magnetic susceptibility passes through a weak maximum near 100 K [17], which is typical of mixed-valence materials. Analysis of the susceptibility data indicates that the characteristic energy scale in δ-Pu is T_K~250 K [17]. Within the framework of the Anderson-impurity model [18], this value of $T_K=(N-1)\pi R/6\gamma=$ 250 K, where R is the gas constant, γ is the electronic specific heat and N is the ground state degeneracy, this implies that $N=4$. Together, these physical properties establish δ-Pu as a correlated-electron metal with a characteristic energy scale approximately one order of magnitude larger than $T_K \cong 25$ of $\mathrm{CeRh}_{2-x}\mathrm{Ru}_x\mathrm{Si}_2$ [6].

Disorder in Pu is unavoidable because of self-damage produced by radioactive decay. Attempts to establish ground state properties of δ-Pu are complicated further by the need to stabilize this phase by chemical substitutions. Even in relatively small amounts, some of these substitutions, e.g., Ga and Al, cause relatively large decreases in the cell volume. For example, increasing Ga content from 2 to 5 at.% decreases the average fcc cell volume by ~2% [19]. Electronic Gruneisen parameters of Ce-based mixed-valence materials having a characteristic energy scale comparable to that of δ-Pu are of the order of 10 [13]. For a 2% volume change, this implies a 20% change in the characteristic scale. The "chemical pressure" produced locally around a Ga impurity is possibly even larger, with a correspondingly larger change in T_0. Given the role of hybridization disorder in $\mathrm{CeRh}_{2-x}\mathrm{Ru}_x\mathrm{Si}_2$, it seems likely that disorder in δ-Pu could have a similar, though possibly less pronounced, effect that should not be disregarded in attempts to understand the physical properties of δ-Pu. An interesting case might be the curious change in sign of the thermal expansion coefficient with increasing content of stabilizing elements. As an example, we have used Eqs. (3) and (4) to calculate the specific heat and thermal expansion coefficient for a system with an average $T_K=$ 250 K and various degrees of disorder. Results are shown in Fig. 3. With no disorder, Eq. (3) reproduces the measured electronic specific heat of δ-Pu (γ~50 mJ mol^{-1} K^{-2}). Assuming an approximately 30% width in the distribution of T_K values (i.e. a few at.% Ga) gives little change in the magnitude or temperature dependence of C_m/T or β/T. However, increasing the distribution width to ~70% (estimated to correspond to ~10 at.% Ga) substantially changes these quantities.

Acknowledgements

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