

Anomalous Pressure Dependence of the Kadowaki-Woods Ratio and Crystal-Field Effects in Mixed-Valence YbInCu₄

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The mixed-valence compound YbInCu₄ was investigated by electrical resistivity and ac specific heat at low temperatures and high pressures. At atmospheric pressure, its Kadowaki-Woods (KW) ratio A/γ^2 is 16 times smaller than the universal value $R_{KW}(= 1.0 \times 10^{-5} \mu\Omega \cdot \text{cm} \cdot \text{mol}^2 \cdot \text{K}^2 \cdot \text{mJ}^{-2})$, but sharply increases to $16.5R_{KW}$ at 27 kbar. The pressure-induced change in the KW ratio and deviation from R_{KW} are analyzed in terms of the change in f -orbital degeneracy N and carrier density n . This analysis is further supported by a dramatic change in residual resistivity ρ_0 near 25 kbar, where ρ_0 jumps by a factor of 7.

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At low temperatures, strongly correlated metals exhibit an enhanced electronic specific heat that is a measure of the density of electronic states at the Fermi energy $N(E_F)$, which results from hybridization of nearly localized and ligand electrons. Scattering of electrons within this strongly correlated Fermi-liquid state is characterized by an electrical resistivity that increases from $T = 0$ as temperature squared, that is, $\rho(T) = \rho(T = 0) + AT^2$. Kadowaki and Woods [1] showed that the ratio of the T^2 resistivity coefficient to specific heat Sommerfeld coefficient γ assumed a common value $A/\gamma^2 = R_{KW} = 1.0 \times 10^{-5} \mu\Omega \cdot \text{cm} \cdot \text{mol}^2 \cdot \text{K}^2 \cdot \text{mJ}^{-2}$ for a diverse set of strongly correlated materials with γ values ranging by 2 orders of magnitude. YbInCu₄, which has a low-temperature γ well within the range of these other materials, is an interesting exception to this common ratio. Such departures from the usual value of R_{KW} challenge Fermi-liquid predictions for strongly correlated systems [2].

At temperatures above $T_v = 42$ K, YbInCu₄ is characterized by a Curie-Weiss temperature dependence in magnetic susceptibility and a semimetallic behavior in transport measurements due to its localized $4f$ electrons [3–5]. At T_v , there is a first-order isostructural valence transition accompanied by a volume increase of +0.5%. In contrast to the trivalent configuration of Yb's $4f$ electrons above T_v , the volume expansion induces strong charge hybridization, a change in Yb's valence from 3+ at $T > T_v$ to a mixed-valence value of 2.9+ below T_v [3], and an enhanced Pauli-like susceptibility corresponding to a modestly large $\gamma = 50 \text{ mJ/mol} \cdot \text{K}^2$ [6]. The T^2 coefficient of resistivity at $T \ll T_v$, however, is much smaller than anticipated by the universal value R_{KW} . Decreasing the cell volume of YbInCu₄ by applied pressure stabilizes the high-temperature $4f^{13}$ configuration to progressively lower temperatures and eventually drives T_v to $T = 0$ near 25 kbar [7], thereby enabling systematic exploration of the origin of the anomalous Kadowaki-Woods ratio that has been observed in other mixed-valence Yb and Ce-based compounds [8]. In this Letter, we report a pressure-induced

KW-ratio change of YbInCu₄ from $0.063R_{KW}$ at $P = 0$ kbar to $16.5R_{KW}$ at $P = 27$ kbar and show that the pressure dependence of the KW ratio and deviation from R_{KW} are due to the change in f -orbital degeneracy N and carrier density n . This conclusion is further supported by a dramatic change in residual resistivity ρ_0 near 25 kbar, where ρ_0 jumps by a factor of 7.

Single crystals of YbInCu₄ were obtained from an In-Cu flux method as described elsewhere [9]. Hydrostatic pressure was achieved by using a hybrid Be-Cu/NiCrAl clamp-type pressure cell with silicone fluid as a transmitting medium. The absolute value of pressure at low temperatures was obtained by measuring the superconducting transition temperature of a tin manometer. The resistivity ρ of YbInCu₄ was measured by a standard four-point method with a LR-700 ac resistance bridge (Linear Research). At ambient pressure, ρ has a very narrow mixed-valence-transition region, $\Delta T \leq 1$ K, and a large resistivity ratio, $\rho(T_{v+})/\rho(T_{v-}) \approx 13$, suggesting that the analyzed crystal is of high quality [9]. Here, $\rho(T_{v+})$ is the resistivity at temperatures just above T_v and $\rho(T_{v-})$, below T_v .

In Fig. 1(a), we show the resistivity of YbInCu₄ as a function of temperature at several pressures on a log-log scale. The valence-transition temperature T_v is rapidly suppressed by applying pressure, $dT_v/dP \approx -1.7$ K/kbar, as reported in transport and thermodynamic measurements [10–12], and goes to zero near 25 kbar. At $P = 27$ kbar, there is no clear drop in ρ that can be attributed to a valence transition. The temperature derivative of the resistivity, surprisingly, reveals a scaling behavior among different pressure data [Fig. 1(b)]. Three distinct regimes in $d\rho/dT$ are identified by a sharp change in the slope at T_v and 32 K: regime I for $T > 32$ K, regime II for $T_v < T < 32$ K, and regime III for $T < T_v$.

In the high-temperature phase (regime I), the electrical resistivity can be accounted for by phonon ρ_{ph} and spin-dependent scattering processes ρ_{mag} : $\rho = \rho_0 + \rho_{ph}(T) + \rho_{mag}(T) = \rho_0 + bT - c \ln T$. The good fit of the above model and a shallow resistivity minimum observed at

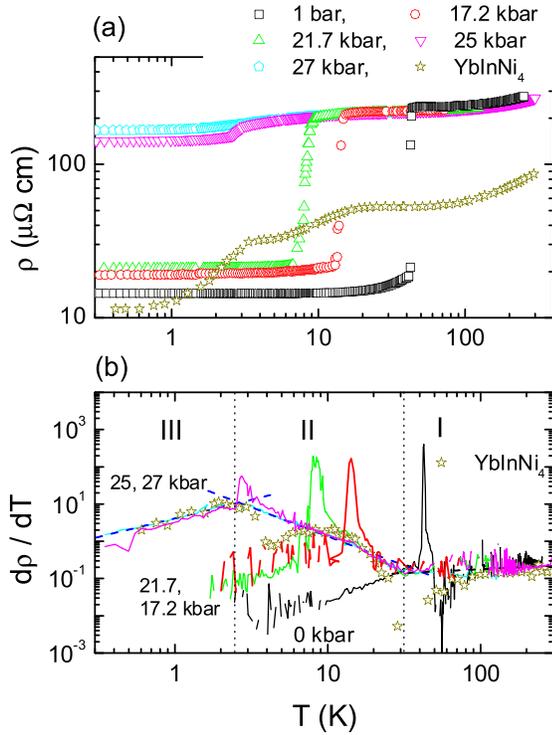


FIG. 1 (color online). (a) Resistivity vs temperature on a log-log scale of YbInCu₄ at different pressures. For comparison, ρ of YbInNi₄ at 1 bar is shown as open stars. (b) Temperature derivative of the resistivity $d\rho/dT$. For clarity, only a few representative data sets are shown. The dashed lines in regimes II and III represent $1/\sqrt{T}$ and T^2 behaviors, respectively.

55 K and ambient pressure (not shown here) signify the importance of Kondo interactions in this compound. The resistivity slope is almost independent of temperature.

For all pressures $P \geq 17.2$ kbar, where $T_v < 32$ K, the resistivity exhibits a significant increase in slope below 32 K. This temperature is of the same order as the crystal-line electric field (CEF) splitting 3.2 meV found in the high-temperature trivalent state by inelastic neutron scattering measurements in YbInCu₄ [13]. From neutron scattering measurements [13], the stable trivalent compound YbInNi₄ exhibits essentially identical crystal-field splitting. The deexcitation of the excited crystal-field level causes a broad shoulder near 20–30 K in the resistivity of YbInNi₄ [Fig. 1(a)] which gives rise to the sharp increase in $d\rho/dT$ below 32 K [Fig. 1(b)]. The sharp drop in ρ below 3.2 K in YbInNi₄ is due to ferromagnetism. The scaling behavior observed in Fig. 1(b) in region II is thus a property of the high-temperature ($T > T_v$) trivalent state which is already present in YbInNi₄. The existence of this scaling behavior also implies that the crystal-field splitting does not change significantly with pressure.

Specific heat measurements of YbInCu₄ also support the conclusion that 32 K is the crystal-field splitting [14]. Figure 2 shows representative specific heat at 27.9 kbar, where a sharp specific heat anomaly due to ferromagnetism

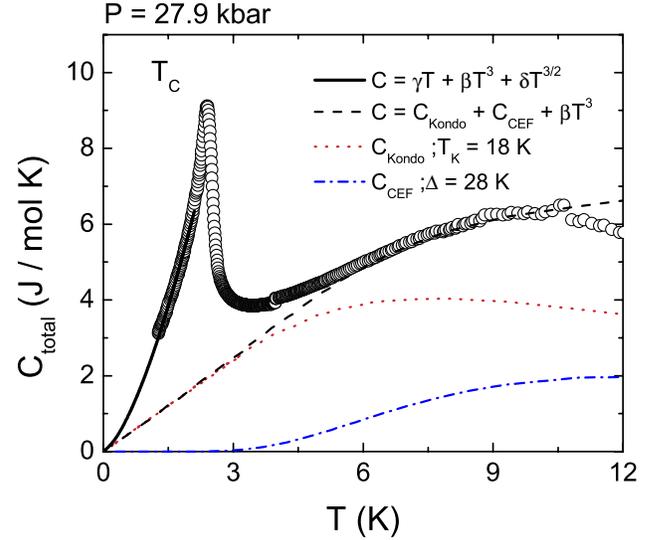


FIG. 2 (color online). Specific heat vs T at 27.9 kbar [14]. The broad maximum near 10 K was interpreted by Kondo (dotted line) and crystal-field (dash-dotted line) effects with a quartet ground state and a doublet excited state. Sommerfeld coefficient γ is obtained by fitting $C_{\text{total}} = \gamma T + \beta T^3 + \delta T^{3/2}$ below $T_c (= 2.5$ K), where the third term is due to magnon contributions.

occurs at 2.5 K [7] and a broad maximum near 10 K is attributable to the combination of Kondo (dotted line) [15] and crystal-field (dash-dotted line) effects. The best fit to the broad maximum was obtained with Kondo temperature $T_K = 18$ K and crystal-field splitting $\Delta = 28$ K with a quartet ground state. A Sommerfeld coefficient $\gamma (= 110 \pm 50$ mJ/mol \cdot K²) is obtained from a least squares fit to data below T_c (solid line).

In the low-temperature phase below T_v (regime III), the temperature dependence of ρ shows typical Fermi-liquid behavior: $\rho = \rho_0 + AT^2$. In Fig. 3(a) we show scaling of the normalized resistivity $\Delta\rho/AT_0^2$ versus $(T/T_0)^2$. Here, $\Delta\rho = \rho(T) - \rho_0$ and T_0 is the highest temperature where the T^2 dependence is obeyed. The scaling temperature T_0 is typically associated with a coherence temperature T_{co} , which is proportional to the Kondo temperature, i.e., $T_{\text{co}} \propto T_K$ [16,17]. It is interesting to note that the presence of the mixed-valence transition changes the resistivity behavior above T_0 : the normalized resistivity deflects upward for $P \leq 25$ kbar, while it deviates downward for $P > 25$ kbar. YbInNi₄ whose ground state is ferromagnetic follows the 27 kbar data of YbInCu₄.

The pressure dependence of the residual resistivity $\rho_0(P)$ obtained from the T^2 scaling is displayed in Fig. 3(b). For $P < 25$ kbar, ρ_0 increases from 14.4 at $P = 0$ to 20.9 $\mu\Omega \cdot \text{cm}$ at $P = 21.7$ kbar. The increase in ρ_0 over this pressure interval is comparable to that of other heavy fermion compounds and suggests that the residual scattering is not simply due to potential scattering from impurities or lattice disorder, but involves the Yb-4*f* elec-

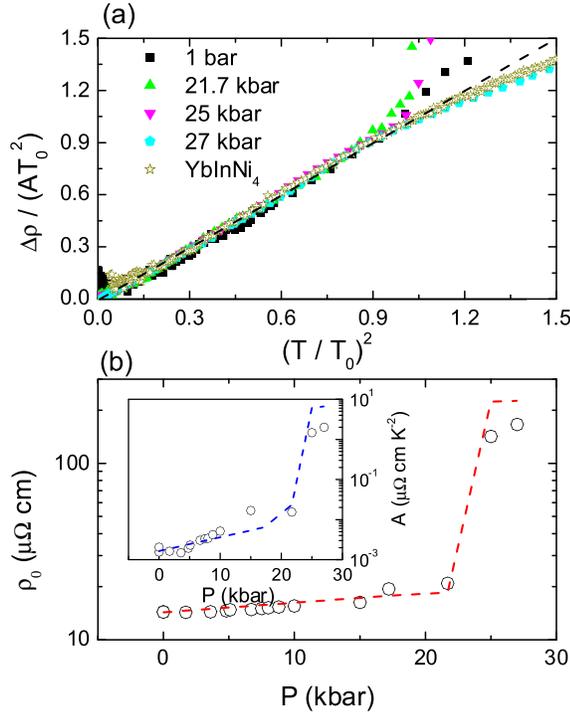


FIG. 3 (color online). (a) Normalized resistivity of YbInCu₄ vs $(T/T_0)^2$ at low temperatures and various pressures, where T_0 is the highest temperature over which ρ obeys a T^2 dependence, $\Delta\rho = \rho(T) - \rho(T = 0)$, and A is the T^2 coefficient. The dashed line is a guide to the eye. (b) Pressure dependence of the residual resistivity on a semilog scale. The dashed line is a fit to Eq. (1). Inset: pressure dependence of A on a semilog scale. The dashed line is a fit to Eq. (2) (see text).

trons [18]. When lattice periodicity is disrupted by disorder in Yb or In sites of YbInCu₄ [9], the scattering phase shift of the Yb-4*f* electrons fluctuates, resulting in a finite resistivity at $T = 0$ K [19,20]:

$$\rho_0 = \frac{G}{n^{1/3}} \sin^2(\pi n_f / N), \quad (1)$$

where N is the effective f -orbital degeneracy and G is a prefactor that takes into account the pressure effects of the hybridization strength. Pressure dependence of the effective 4*f* hole occupation number n_f of YbInCu₄ was obtained from Ref. [21] up to 16 kbar. For $P > 16$ kbar, n_f was extrapolated with an assumption that n_f at 25 kbar is equal to that ($= 0.94$) in the high-temperature phase at $P = 0$ kbar [21]. For $T < T_v$, the effective degeneracy N is $8 (= 2j + 1)$, as expected from the strongly hybridized mixed-valence state and from the absence of CEF excitations in neutron scattering [13], and where j is the total angular momentum ($= 7/2$). Even though the carrier density n is a function of pressure, for simplicity, we used 2.2 per formula unit below 25 kbar and 0.07 above that pressure [22]. The best fit was obtained with $G(P) \propto (1 + 0.005P)$ [dashed line in Fig. 3(b)], which is simi-

lar to that of YbInNi₄ [23]. The positive slope in ρ_0 of the Yb-based compounds, $d\rho_0/dP > 0$, reflects the 4*f*-hybridization effects, which make the slope negative in Ce-based compounds, electron analogs of Yb-based compounds.

At $P = 25$ kbar, there is a pronounced jump in ρ_0 by a factor of 7. Once the characteristic energy scale for spin fluctuations decreases with applied pressure below the first excited CEF level, the effective degeneracy will decrease and, consequently, the residual resistivity increases sharply. When the effective degeneracy changes from 8 to 4, the sharp increase is well explained by Eq. (1) [dashed line in Fig. 3(b)]. Further support for a change in degeneracy comes from the pressure dependence of the Kondo temperature T_K and crystal-field scale T_{CEF} [see Fig. 4(a)]. T_K decreases with pressure, while T_{CEF} is essentially independent of pressure. T_K , indeed, becomes smaller than T_{CEF} near 25 kbar, indicating that crystal fields which lift the full j manifold degeneracy, are important for $P \geq 25$ kbar. Values of T_K plotted in Fig. 4(a) were obtained

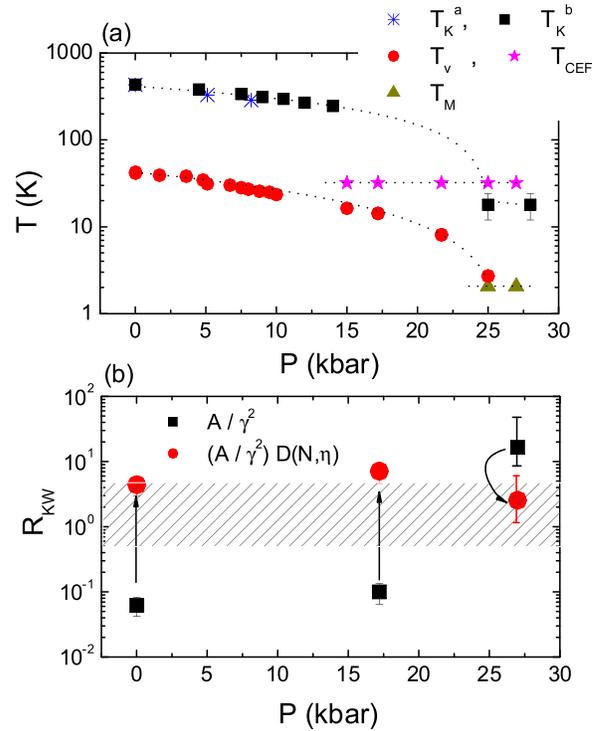


FIG. 4 (color online). (a) T - P phase diagram on a semilog scale. T_M is a magnetic ordering temperature from χ_{ac} (not shown) and T_v is the valence-transition temperature. The Kondo temperature T_K^a is from Ref. [11] and T_K^b from Ref. [21]. For $P > 25$ kbar, T_K is obtained from specific heat measurements [14]. The dotted line that connects T_K 's is a guide to the eyes [25]. (b) The pressure dependence of the KW ratio A/γ^2 is shown in squares and the renormalized ratio $(A/\gamma^2)D(N, \eta)$, in circles. The y-axis unit is $R_{\text{KW}} (= 1.0 \times 10^{-5} \mu\Omega \cdot \text{cm} \cdot \text{mol}^2 \cdot \text{K}^2 \cdot \text{mJ}^{-2})$. The hatched band is from 0.5 to $5R_{\text{KW}}$ within which most of heavy fermions are located.

from Ref. [11,21] for $P < 25$ kbar and specific heat measurements for $P \geq 25$ kbar [14].

A change in ground state degeneracy is also manifested in the pressure dependence of the T^2 coefficient A . The gradual increase in A with pressure turns into a jump at 25 kbar. In the inset of Fig. 3(b), we compare experimental results to predictions for a lattice Anderson model [24]:

$$A = \frac{\kappa}{N^2} \frac{n^{-1/3}}{T_K^2}, \quad (2)$$

where κ is constant and n is carrier density. Best results were obtained when the degeneracy N changes from 8 to 4 near 25 kbar, which is consistent with the quartet ground state claimed both from inelastic neutron scattering [13] and from thermodynamic measurements [6].

Recently, a correlation between the KW ratio and a f -orbital degeneracy N of heavy fermion compounds was theoretically explored by Kontani [2] who predicted:

$$\frac{A}{\gamma^2} \approx D^{-1}(N, \eta) R_{\text{KW}} = \frac{2R_{\text{KW}}}{N(N-1)} \frac{\alpha}{\eta^{4/3}}, \quad (3)$$

where the lattice spacing $a = \alpha a_0$ with $a_0 = 1 \times 10^{-8}$ cm and carrier density $n = \eta/a^3$. When the degeneracy N changes, it not only changes the electronic density of states but also the scattering rates, renormalizing both quantities A and γ . Figure 4(b) shows the KW ratio before (squares) and after (circles) taking into account $D(N, \eta)$. The anomalously small measured value of A/γ^2 ($0.063R_{\text{KW}}$) at $P = 0$ kbar increases to $16.5R_{\text{KW}}$ at $P = 27$ kbar, where the effective degeneracy changes from an octet to a quartet. When both the degeneracy factor and carrier density are considered (circles), $(A/\gamma^2)D(N, \eta)$, the renormalized ratios at all pressures converge to the characteristic value found in most heavy fermion compounds [1], delineating the relationship between the effective degeneracy and the small value of the KW ratio.

In summary, we have reported an anomalous pressure dependence of the KW ratio of YbInCu_4 . At $P = 0$ kbar, the KW ratio, A/γ^2 , is 16 times smaller than the universal value (R_{KW}), but sharply increases to $16.5R_{\text{KW}}$ at 27 kbar. The pressure-induced change in the KW ratio and deviation from R_{KW} are analyzed in terms of the change in f -orbital degeneracy N and carrier density n , which was further supported by a pronounced change in the residual resistivity at 25 kbar. We claim that there no longer should be a distinction between ‘‘anomalous’’ and ‘‘normal’’ values of the KW ratio; rather, both the smaller and more commonly observed values are a direct consequence of carrier density and magnetic degeneracy of f ions.

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