# Magnetic-field, pressure, and temperature scaling of the first-order valence transition in pure and doped YbInCu$_4$

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We report measurements of the high-field ($H \leq 30$ T) magnetoresistance $R(H,T)$ of pure and doped YbInCu$_4$. A hysteretic transition is observed which we take to be the field-induced variant of the first-order valence transition observed at 42 K in YbInCu$_4$ for $H=0$ T. Applied pressure suppresses the valence transition to lower temperature. By properly scaling the ($H_v$, $T_v$) data extracted from the resistance measurements, we can collapse all of the pressure-dependent data, as well as that from doped variants of YbInCu$_4$ at ambient pressure, onto a universal $H$-$T$ phase diagram. This suggests that a single energy scale is associated with the valence transition. [S0163-1829(97)00225-7]

YbInCu$_4$ has attracted much recent attention because it is the only known stoichiometric compound that undergoes a first-order isostructural valence transition at ambient pressure.[1–10] At high temperature ($T > 50$ K) Yb appears to be essentially trivalent, displaying Curie-Weiss susceptibility with a paramagnetic moment near the free-ion value of 4.5 $\mu_B$. At the first-order valence transition ($T_v = 42$ K) the Yb valence is reduced to approximately 2.9 (as estimated by x-ray-absorption and lattice constant measurements[1]), with a consequent increase in lattice volume of 0.5% and a reduction in magnetic susceptibility and spin-disorder scattering.[6] High-resolution neutron powder-diffraction studies confirm that the first-order transition is an isostructural one, with YbInCu$_4$ retaining its $C15b$ structure at all temperatures.[8] The physics here mimic the $\gamma$-$\alpha$ transition in elemental Ce.[11] However, because the valence transition occurs at lower temperature and at ambient pressure and there is no intervening phase (e.g., $\beta$-Ce), YbInCu$_4$ is a ''cleaner'' system experimentally. The physical origin of the transition is generally taken to be the strong volume dependence of the Kondo temperature as explained, for example, by the Kondo volume collapse model.[7,12] Recently, however, Freericks and Zlatic have suggested that a Falicov-Kimball model, in which only a fraction of Yb sites are active, may be more appropriate.[13]

Because of the strong volume dependence of the valence transition (as evidenced by the lattice constant and bulk modulus anomalies associated with the transition[2,6]) as well as its rather low critical temperature, applied pressure and external magnetic fields promise to shed valuable light on the details of the physics of YbInCu$_4$. In fact, much work has already been done in this regard.[1,5,14–17] Measurements of magnetization and forced magnetostriction provide compelling evidence that the observed field-induced transition is precisely the same valence transition as observed as a function of temperature at ambient field.[5,14] An increase in Yb valence, as deduced from the measured effective magnetic moment per Yb and from the measured change in sample volume, of approximately the same magnitude as the decrease in valence discussed above is observed.

Applied pressure pushes the valence transition to lower temperature.[1,5,16,17] This is presumably because under pressure the smaller Yb$^{3+}$ configuration is favored over the larger Yb$^{2+}$ one. The initial rate of depression of $T_v$ is approximately 2 K/kbar and for applied pressures up to 10 kbar, the resistive transition remains first order despite the reduced transition temperature.[18] It is not year clear whether the transition temperature can be suppressed all the way to $T=0$ or whether the $P$-$T$ phase diagram ends in a lower critical point as is the case for some variants of $\gamma$-$\alpha$ Ce.[19]

However, many of these previous studies suffered from sample uncertainty. The reported transition temperature for YbInCu$_4$ varies from 40–60 K, and many of the observed transitions have been less than steplike, even at ambient pressure and field. Thus, when the transition is broadened or lowered in temperature, it is hard to separate the intrinsic effect from extrinsic ones, making the identification of the transition temperature and the order of the transition more difficult. Recently, we have established a protocol for synthesizing single crystals of YbInCu$_4$ which yields sharper transitions than previously reported ($T_v = 42 \pm 1$ K, with transition widths $\leq 1$ K),[6,7] and we have demonstrated a correlation between disorder and transition temperature that suggests that our flux-grown single crystals are of the highest quality.[8]

Here we report resistance measurements as a function of pressure, temperature, and magnetic field in pure and doped YbInCu$_4$ using our high-quality single crystals. A sharp and hysteretic transition is observed as a function of applied magnetic field, and from these data we generate a magnetic field-temperature phase diagram for YbInCu$_4$. For stoichiometric samples under applied pressure and for Y-, Lu-, and Ag-doped samples which still possess a first-order valence transition, similar phase diagrams have also been generated. By properly scaling these results, we can collapse the data onto a single curve of the form $[H_v/H_v(T=0)]^2 + [T_v/T_v(H=0)]^2 = 1$, where $H_v = H_v(T)$ and $T_v = T_v(H)$ are the critical field and critical temperature, respectively, for
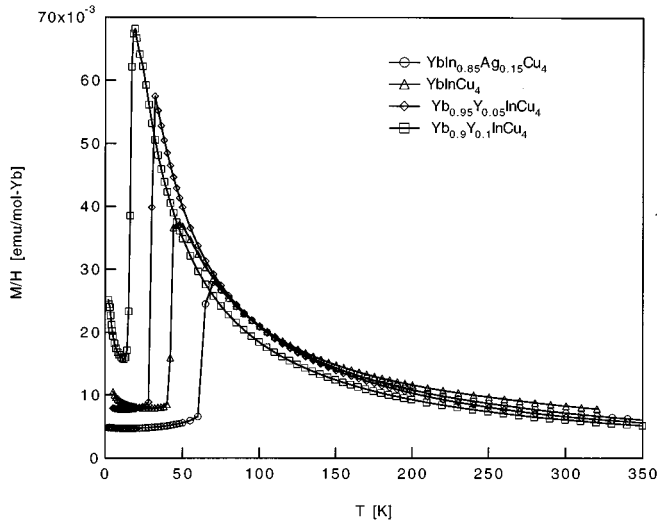
FIG. 1. Magnetic susceptibility versus temperature for representative samples used in this study. Note the sharp drop in susceptibility at the valence transition. The lines are guides to the eye, and the small upturns at lowest temperature for some samples are extrinsic Curie tails.



FIG. 2. Resistance as a function of applied field at various fixed temperatures for YbInCu$_4$ under an applied pressure of 6 kbar. Field sweeps were performed at 5, 10, 12, 14, 16, 18, 20, 22, 24, 26, 27, 28, 29, and 30 K (in order of decreasing transition field). At a given temperature, data for both increasing and decreasing field sweeps are shown. The valence transition occurs at higher field for positive field sweeps.

the valence transition, demonstrating the existence of a law of corresponding states for the first-order transition and suggesting that the effect of magnetic field is simply to supply Zeeman energy to the transition. Finally, we speculate as to the origin of this simple magnetic-field coupling and relate it to the much stronger effect of applied physical pressure.

Single crystals of stoichiometric and doped YbInCu$_4$ were grown from InCu fluxes as previously described.[7] Doping YbInCu$_4$ with Y or Lu drives the valence transition to lower temperature, an apparent dilution effect. Substituting Ag for In leads to an increase in valence transition temperature, at least for small Ag concentrations. At high Ag concentration typical mixed-valence behavior is recovered. A crossover from first-order to continuous behavior is observed for both Yb- and In-site doping, suggesting that there is both an upper and lower critical point in the phase diagram. The detailed composition-temperature phase diagram of YbInCu$_4$ has been discussed elsewhere.[7,20] All of the measurements reported here were made with single crystals that displayed sharp and hysteretic resistive transitions at ambient pressure in the earth's field. In Fig. 1 we show the low-field static susceptibility $\chi(T)$ at ambient pressure for representative single crystals used in this study.

The $R(H,T)$ measurements were made using the standard four-probe ac technique in the 30 T resistive magnets at the National High Magnetic Field Laboratory (NHMFL).[21] These magnets provide dc fields that are uniform to 0.05% over a 1 cm diameter spherical volume. Care was taken to ensure accurate temperature calibration at high fields, as well as to rule out field-sweep rate-dependent effects. Typical field sweeps were performed at a rate of 5 T/min, and temperature stability was better than 0.1 K over the course of a complete 12-min scan. The pressure measurements were performed in hydrostatic Be-Cu clamps. The effective pressure at low temperature was measured using a lead manometer and was assumed to be independent of temperature over the
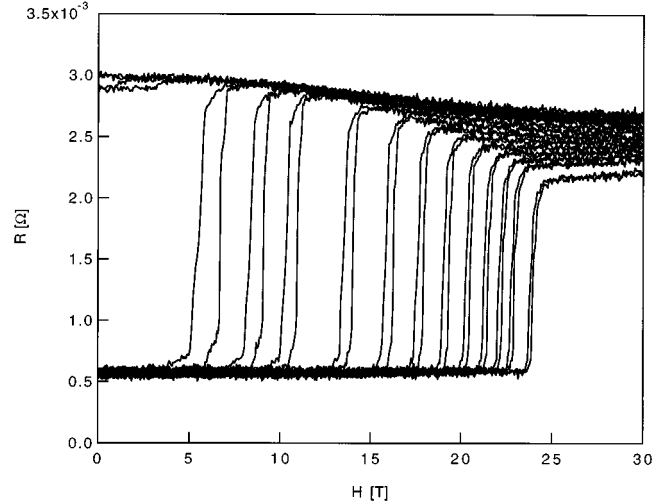
temperature range of interest (2 K$\leqslant T \leqslant$50 K).[22] We estimate the absolute uncertainty in reported pressure values to be 0.5 kbar.

In Fig. 2 we show plots of resistance as a function of magnetic field for both positive and negative field sweeps at various fixed temperatures for a sample of YbInCu$_4$ under an applied pressure of 6 kbar. A clear field-induced transition from a low-resistance state to a high-resistance one is observed. This effect is consistent with what is observed in the temperature-dependent resistivity at ambient field and pressure and is associated with a reduction of spin-disorder scattering in the low-temperature, low-field state.[7] The transition occurs at higher fields for increasing-field sweeps as compared to decreasing-field sweeps. The width of the hysteresis increases with increasing temperature. Although the origin of this effect is not clear, it may be due to thermal fluctuation effects associated with the proximity of the ambient field transition. As compared to the size of the steplike change in resistance, all other magnetoresistive effects are small. However, the resistance at high field does appear to have an appreciable temperature dependence in the high-resistance Yb$^{3+}$ state, as evidenced by the steady drop in $R(H=30$ T) for decreasing temperature.

Similar data for $R(H,T)$ have been obtained for YbInCu$_4$ under ambient and applied pressure (2.4 and 10 kbar, in addition to the 6-kbar data shown in Fig. 2), as well as for Ag-, Lu-, and Y-doped samples. The ambient-field dependence of the valence transition temperature with pressure is qualitatively consistent with previously published work.[5,15−17] These data and their implications for the thermodynamics of the first-order valence transition will be discussed elsewhere.[18]

From data such as in Fig. 2, one can identify an $H_v^+$ and an $H_v^-$ (the critical field for positive and negative field sweeps, respectively, taken as the point of maximum derivative) for a given sample at fixed pressure and temperature.
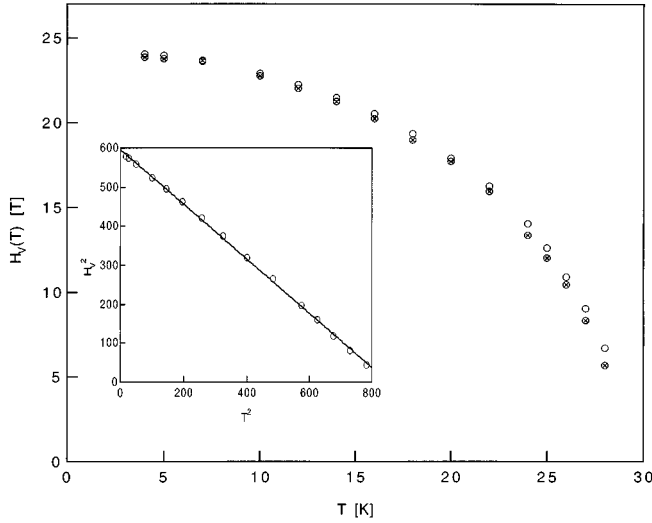
FIG. 3. $H_V{}^+$ (open symbols) and $H_v{}^-$ (filled symbols) as a function of temperature, extracted from the data of Fig. 2. See text for details. The inset shows the linear relationship between $H_v{}^2$ (for clarity, only the the $H_v{}^+$ data are plotted) and $T^2$.
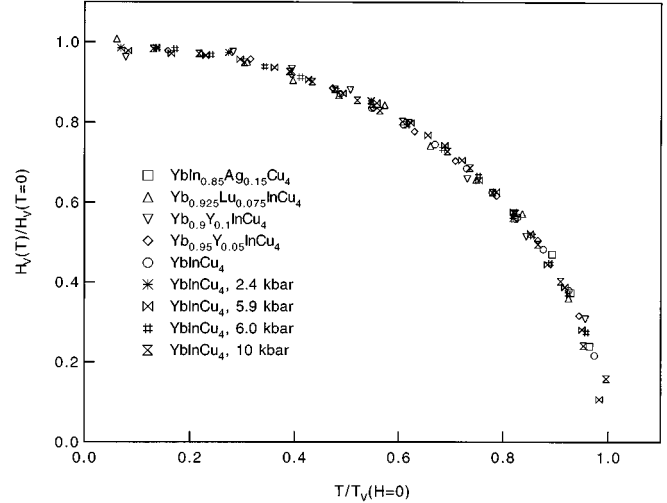


FIG. 4. $H_v(T)/H_v(T=0)$ versus $T_v(H)/T_v(H=0)$ for a variety of samples. The $(H_v,T_v)$ data for a given sample can be collapsed to a universal curve by proper scaling. The data for YbInCu$_4$ at 6.0 kbar were taken with a different crystal than all of the other YbInCu$_4$ data which were obtained with the same crystal.

These data are shown in Fig. 3. We have verified, by performing temperature sweeps at fixed field, that for a given sample an $(H_v,T_v)$ data point does not depend on whether field or temperature is being swept. We[23] and others[14,15] have also measured magnetization as a function of applied field and from such data obtain quantitatively similar phase diagrams.

The data in Fig. 3 reveal that the $(H_v,T_v)$ data points satisfy an elliptic equation.[15] By plotting the data as $H_v^2$ vs $T_v^2$ a linear fit can be obtained and from these fits $H_v(T=0)$ and $T_v(H=0)$ can be extracted (inset, Fig. 3). As would be expected, the fitted $T_v(H=0)$ values agree quantitatively with those determined by zero-field resistance measurements. Additionally, although the magnetic field required to induce the valence transition for fixed temperatures less than 20 K in stoichiometric YbInCu$_4$ under ambient pressure is greater than presently available dc fields, we have performed measurements in pulsed magnetic fields of up to 50 T at temperatures as low as 1.7 K. The observed value of $H_v(T=1.7$ K$)=33$ T (data not shown) is consistent with the extrapolated value $[H_v(T=0)=34$ T$]$ for pure YbInCu$_4$ at ambient pressure.

If the $(H_v,T_v)$ data are scaled by the $H_v(T=0)$ and $T_v(H=0)$ for a given sample, all of the data from each of the samples discussed above can be made to collapse onto a single universal curve which is well described by $[H_v(T)/H_v(T=0)]^2+[T_v(H)/T_v(H=0)]^2=1$. These data are shown in Fig. 4—for clarity, only $H_v{}^+$ values (i.e., data for positive field sweeps) are shown. The extracted values of $H_v(T=0)$ and $T_v(H=0)$ for each of these samples is given in Table I. Although the precise physical description of this phase transition is unclear, a scaling relationship between thermal and Zeeman energy is apparent which is independent of physical pressure or doping and points to a single energy scale governing this first-order valence transition. This also suggests the existence of a law of corresponding states associated with the first-order transition.[24] Furthermore, because the scaling relationship does not vary with doping, single ion

effects, rather than coherence-induced effects, are implicated as the microscopic mechanism underlying the transition.

The relationship between thermal energy and Zeeman energy can be examined by comparing $H_v(T=0)$ and $T_v(H=0)$ for a given sample. In particular, by equating $k_BT_v=a\mu_BH_v$, we find $a=1.8\pm0.1$ for each of the samples in Fig. 4. Thus, not only is there a single energy scale for the valence transition but also the relative strength of magnetic-field coupling to the transition is independent of doping or physical pressure within our resolution. Naively, one might expect $a$ to correspond to the ''$g$ value'' of the ion or excitation to which the field is coupled. However, $g=1.8$ corresponds to neither the ubiquitous $g=2$ of $S=1/2$ excitations or the $g=8/7$ expected for $J=7/2$ Yb$^{3+}$. The existence of a cubic crystal field breaks the eightfold degeneracy of the $J=7/2$ ground state. However, the $g$ values calculated for the $\Gamma_8$ ground state of YbInCu$_4$ in the high-temperature state (as determined by inelastic neutron-scattering measurements[25]) are in no better agreement with our data.[26] Furthermore, inelastic neutron-scattering measurements[10,25] suggest that a crystal-field description of the low-temperature state of YbInCu$_4$ is inappropriate.

TABLE I. $H_v(T=0)$ and $T_v(H=0)$ extracted from magnetoresistance measurements for each of the samples shown in Fig. 4. See text for details.

| Sample | $H_V(T=0)$ | $T_V(H=0)$ |
|---|---|---|
| YbInCu$_4$ | 34.3 | 41.1 |
| YbInCu$_4$, 2.4 kbar | 28.4 | 36.6 |
| YbInCu$_4$, 5.9 kbar | 24.3 | 30.5 |
| YbInCu$_4$, 6.0 kbar | 24.4 | 29.2 |
| YbInCu$_4$, 10 kbar | 18.8 | 23.1 |
| YbIn$_{0.85}$Ag$_{0.15}$Cu$_4$ | 53.3 | 70.0 |
| Yb$_{0.925}$Lu$_{0.075}$InCu$_4$ | 19.0 | 22.7 |
| Yb$_{0.9}$Y$_{0.1}$InCu$_4$ | 15.1 | 17.8 |
| Yb$_{0.95}$Y$_{0.05}$InCu$_4$ | 25.7 | 31.7 |

The Kondo volume collapse model[12] suggests that the valence transition in $\gamma$-$\alpha$ Ce occurs at a temperature near the Kondo temperature. This also appears to be true in YbInCu$_4$ ($T_v = 42$ K and the high-temperature Kondo temperature[7] is 20 K for stoichiometric YbInCu$_4$ at ambient pressure in the earth's magnetic field). If this identification were to remain true as a function of field, our data suggest that $T_K^2 \alpha H^2$; however, we are unaware of theoretical calculations that predict such a field dependence of $T_K$.[27] An empirical expression of the form $T_K(H) = T_K(H=0)\{1 + [\mu_B/k_B T_K(H=0)]^2\}^{1/2}$ has been proposed for the related compound YbAgCu$_4$.[28] This expression predicts an elliptical relationship between $T_K$ and $H$, the same functional form as our result for $T_v(H)$, but it implies, consistent with experiment,[28] that $T_K$ increases with field whereas if one assumes that $T_v = T_K$, our data suggest that $T_K$ decreases with field. Further theoretical study is required to establish the possible origins of this functional dependence and to understand how the sign of the coupling might vary from compound to compound.

Finally, it is interesting to note that the combined thermal and Zeeman energy of the valence transition in stoichiometric YbInCu$_4$ at ambient pressure (3.5 meV) does correspond remarkably well to the amount of energy associated with the volume expansion: $E = 1/2 B V (\Delta V/V)^2$, where $B = 110$ GPa,[2] $\Delta V/V = 0.5\%$, and $V = (7.15 \text{ Å})^3$ per unit cell, gives 3.1 meV. Thus, a fixed energy independent of temperature, magnetic field, or applied pressure seems to be associated with the first-order valence transition. Further work remains to identify the underlying microscopic mechanism that gives rise to such interesting yet simple physics.

[1] I. Felner and I. Nowik, Phys. Rev. B **33**, 617 (1986); I. Felner *et al.*, *ibid.* **35**, 6956 (1987); I. Nowik *et al.*, *ibid.* **37**, 5633 (1988).

[2] B. Kindler, D. Finsterbusch, R. Graf, F. Ritter, W. Assmus, and B. Luthi, Phys. Rev. B **50**, 704 (1994).

[3] T. S. Altshuler, M. S. Bresler, M. Schlott, R. Elschner, and E. Gratz, Z. Phys. B **99**, 57 (1995).

[4] M. Miljak, I. Aviani, and V. Zlatic (unpublished).

[5] J. M. de Teresa, Z. Arnold, A. del Moral, M. R. Ibarra, J. Kamard, D. T. Adroja, and B. Rainford, Solid State Commun. **99**, 911 (1996).

[6] J. L. Sarrao, C. L. Benton, Z. Fisk, J. M. Lawrence, D. Mandrus, and J. D. Thompson, Physica B **223&224**, 366 (1996).

[7] J. L. Sarrao, C. D. Immer, C. L. Benton, Z. Fisk, J. M. Lawrence, D. Mandrus, and J. D. Thompson, Phys. Rev. B **54**, 12 207 (1996).

[8] J. M. Lawrence, G. H. Kwei, J. L. Sarrao, Z. Fisk, D. Mandrus, and J. D. Thompson, Phys. Rev. B **54**, 6011 (1996).

[9] C. Rettori, S. Oseroff, D. Rao, P. G. Pagliuso, G. E. Barberis, J. L. Sarrao, Z. Fisk, and M. F. Hundley, Phys. Rev. B **55**, 1016 (1997).

[10] J. M. Lawrence, S. M. Shapiro, J. L. Sarrao, and Z. Fisk, Phys. Rev. B **55**, 14 467 (1997).

[11] For a review, see J. M. Lawrence, P. S. Riseborough, and R. D. Parks, Rep. Prog. Phys. **44**, 1 (1981).

[12] J. W. Allen and R. M. Martin, Phys. Rev. Lett. **49**, 1106 (1982); see also, J. W. Allen and L. Z. Liu, Phys. Rev. B **46**, 5047 (1992).

[13] J. K. Freericks and V. Zlatic (unpublished).

[14] K. Yoshimura, T. Nitta, M. Mekata, T. Shimizu, T. Sakakibara, T. Goto, and G. Kido, Phys. Rev. Lett. **60**, 851 (1988).

[15] H. Aruga Katori, T. Goto, and K. Yoshimura, J. Magn. Magn. Mater. **140-144**, 1245 (1995), and references therein.

[16] K. Kojima, K. Hiraoka, H. Takahashi, N. Mori, and T. Hihara, J. Magn. Magn. Mater. **140-144**, 1241 (1995), and references therein.

[17] T. Matsumoto, T. Shimizu, Y. Yamada, and K. Yoshimura, J. Magn. Magn. Mater. **104-107**, 647 (1992).

[18] C. D. Immer *et al.* (unpublished).

[19] J. D. Thompson, Z. Fisk, J. M. Lawrence, J. L. Smith, and R. M. Martin, Phys. Rev. Lett. **50**, 1081 (1980).

[20] J. L. Sarrao *et al.* (unpublished).

[21] M. D. Bird, S. Bole, Y. M. Eyssa, B.-J. Gao, and H.-J. Scneider-Muntau, IEEE Trans. Magn. **32**, 2444 (1996).

[22] J. D. Thompson, Rev. Sci. Instrum. **55**, 231 (1984).

[23] A. Lacerda *et al.* (unpublished).

[24] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, Oxford, 1980), Pt., 1 Secs. 81–84.

[25] A. Severing, E. Gratz, B. D. Rainford, and K. Yoshimura, Physica B **163**, 409 (1990).

[26] G. B. Martins (unpublished).

[27] J. M. Lawrence (unpublished). In the limit of small $H/T_K$, one can motivate such a relationship by assuming $T_K(H) \alpha 1/\gamma(H)$, i.e., assuming the constancy of the Wilson ratio with field, and using the Bethe ansatz expression for $M(H)$ [A. C. Hewson and J. W. Rasul, J. Phys. C **16**, 6799 (1983)] to calculate $T_K(H)$. However, such an expression is expected to break down in the regime of $H \sim T_K$, the region of interest for our experiments.

[28] T. Graf, R. Movshovich, , Z. Fisk, and P. C. Canfield, Phys. Rev. B **52**, 3099 (1995).