THE VALENCE INSTABILITY AND ASSOCIATED PHENOMENA in Ce1-xThx

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THE VALENCE INSTABILITY AND ASSOCIATED PHENOMENA in $Ce_{1-x}Th_x$ (*)

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Résumé. — Nous présentons des résultats sur la susceptibilité $\chi(x\ ;\ T)$ et l'équation d'état des alliages $Ce_{1-x}Th_x$. Nous soutenons que les interactions de couplage par l'intermédiaire du réseau et celles dues à l'effet d'écran des électrons sont toutes deux impliquées dans la transition de valence. Le comportement magnétique dans l'état de valence intermédiaire est celui d'un liquide de fermi ayant une bande d'énergie étroite, avec possibilité d'effets dus aux paramagnons. Nous avons observé de grandes valeurs négatives pour les paramètres de Curie-Weiss dans l'état de valence entier qui semblent indiquer la présence d'un échange RKKY qui est lui-même amplifié de façon anormale par la proximité du niveau 4f de l'énergie de Fermi. Le couplage de la résistivité et du moment efficace χT avec le paramètre d'ordre requiert une justification théorique.

Abstract. — We report experimental results for the magnetic susceptibility $\chi(x\ ;\ T)$ and equation of state of $Ce_{1-x}Th_x$. We argue that both lattice-mediated interactions and electronic screening interactions are involved in the valence transition. The magnetic behaviour in the intermediate valence state is that of a narrow band fermi liquid. The Curie-Weiss-like behaviour observed in the integral valence state may reflect valence fluctuations or spin fluctuations arising from the proximity of the 4f level to the fermi energy. The coupling of resistivity and effective moment χT to the order parameter stand in need of theoretical justification.

1. **Introduction.** — The isomorphic α-γ cerium valence transition is a metallic analogue of the liquid-vapor transition. There is a critical point in the P-T plane and density is the order parameter. The following picture of the valence instability has emerged [1] : in the integral valence γ-state the $4f^1$ level at energy E_f is fully occupied ($n_f = 1$) but in close proximity to the $5d^1\ 6s^2$ fermi level ε_F. The transition involves a many-body effect causing E_f to move up to ε_F. In the intermediate valence α-state the 4f level is pinned at ε_F, with fractional occupancy ($n_f \sim 0.4$) ; and it takes on a width Γ due to hybridization with the band states. Recent theories [2] demonstrate that when $\Delta\varepsilon = \varepsilon_F - E_f < \Gamma$ the system manifests at low temperatures as a fermi liquid, even in the presence of enormous intra-atomic coulomb correlation $U \gg \Delta\varepsilon,\ \Gamma$. In particular the susceptibility follows $\chi \sim 1/\Gamma$.

The valence transition can be driven to a $P = 0$ critical point in the x-T plane of the alloy system $Ce_{1-x}Th_x$ [3]. The critical exponents are those of mean-field theory, and a quantitative Van der Waals' equation of state fits the data in the critical region [4]. Resistivity, entropy, effective moment and volume all couple linearly to the order parameter [4]. The mean-field character undoubtedly arises from strong electro-elastic coupling associated with the large volume collapse (15 %) at the transition [5]. The cerium $J = 5/2$ entropy $Nn_f\ kln\ 6$ causes the phase boundary to have finite slope $\Delta T/\Delta x$; this is one of the important differences between cerium and SmS, where $J = 0$ in the integral valence state, and $\Delta T/\Delta x \to \infty$.

Herein we address the following questions : First, does the lattice coupling alone drive the valence transition, or does electron screening also play a role ? Second, does the fermi liquid picture of the intermediate valence state adequately describe the low temperature behaviour ? And third, what effects arise in the integral valence state due to the near degeneracy of the magnetic 4f level to the fermi energy ? To this end we present revised results for the equation of state and new results for the magnetic susceptibility $\chi(x\ ;\ T)$ for $Ce_{1-x}Th_x$ alloys.

2. **Experimental results.** — Sample fabrication, measurement and data analysis were standard ; we refer the reader to ref. [6] for details, reporting here the results, and a discussion of extrinsic limitations of the data.

Utilizing the linear coupling of resistivity ρ to the order parameter we can express the equation of state in terms of $\Delta\rho = \rho - \rho_0$, $\Delta T = T - T_0$, $\Delta x = x - x_0$:

$$A\left(\frac{\Delta\rho}{\rho_0}\right)^3 + B\left(\frac{\Delta x}{x_0}\right)\frac{\Delta\rho}{\rho_0} = \Delta T - D\left(\frac{\Delta x}{x_0}\right). \quad (1)$$

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We present revised values of the parameters, reflecting adoption of a normalization per cerium atom

$$[\rho(T) = (\rho_{\text{total}}(T) - \rho(4.2))/(1 - x)],$$

an improved least-squares routine, and additional data :

$x_0 = 0.265 \pm 0.003$; $\rho_0 = (57 \pm 3)$ $\mu\Omega$-cm/Ce-atom

for

$$0.17 < x < 0.32 ; \quad T_c(x) = T_0 + D(\Delta x/x_0) \pm 3 \text{ K}$$

with

$$T_0 = 148 \text{ K}, D = 13 \text{ K} ; \quad B = (118 \pm 10) \text{ K} ; \quad A \simeq (125 - 290(\Delta x/x_0) \pm 10) \text{ K}$$

for $0.265 < x < 0.321$, $A \sim 60$ K for $0.32 < x < 0.41$. In figure 1 we plot the data in various ways, together

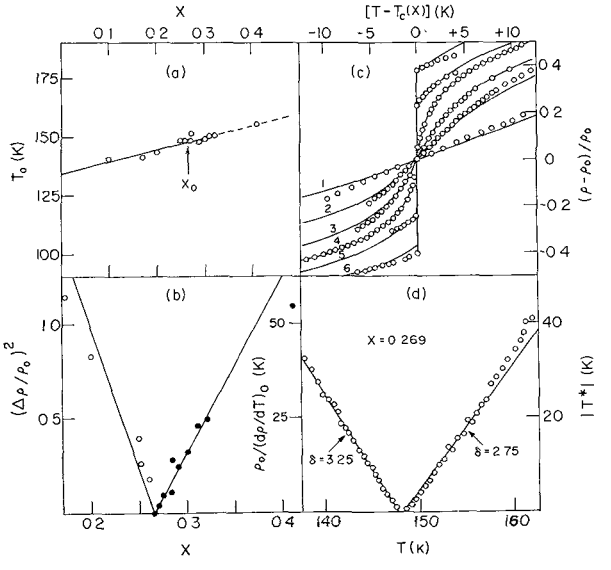

FIG. 1. — Resistivity data for $Ce_{1-x}Th_x$ plotted with the predictions of the equation of state (solid lines). (*a*) Phase boundary, (*b*) squared first-order jumps and inverse maximum derivatives, (*c*) $\Delta\rho$ vs. ΔT for $1.x = 0.411$, $2.x = 0.321$, $3.x = 0.291$, $4.x = 0.269$, $5.x = 0.252$, $6.x = 0.227$, (*d*) $|T^*(T)|$ (see text) for a nearly critical sample.

with the predictions of eq. (1) ; we use $A = 118$ K in this plot. Figure 1*c* makes clear the resemblance between the $\Delta\rho$ vs. ΔT curves and the M vs. H curves in a ferromagnet [5] ; the straight lines in figure 1*b* reflect the mean-field exponents $\beta = 1/2$ and $\gamma = 1$; and in figure 1*d*, by plotting $T^*(T) = \Delta\rho/(\mathrm{d}\rho/\mathrm{d}T)$, we show that for $x \sim x_0$, $(\Delta\rho)^\delta \sim \Delta T$ with $\delta = 3$, the mean field value. (The small asymmetry in δ can be accounted for by including a term $- C\,\Delta T(\Delta\rho/\rho_0)$ on the left in eq. (1), with $C \sim 0.3 \pm 0.2$.)

Extrinsic scatter in these plots undoubtedly arises from the large strain fields associated with the 15 % volume collapse in these polycrystalline samples. In principle the equation of state, based on good statistics, provides an excellent device for characterizing sample quality-inhomogeneity shows up as excessive deviation from the parameters. A small hysteresis ($\Delta T_c \simeq 2$ K) is observed for samples with $x > x_0$ [3] ; this has no effect on the δ exponent but causes the A and B parameters observed on warming cycles to differ by 5-10 % from those observed on cooling. For consistency all values reported here are for cooling cycles. We believe this hysteresis reflects incomplete transformation [7]. A small fraction n_γ of magnetic cerium is retained at 4.2 K, contributing B/T to the low temperature susceptibility where $B = n_\gamma C$ and $C = 5\,760$ emu-K/g-Ce is the $J = 5/2$ Curie constant ; typically $n_\gamma \sim 0.005$. B does not reproduce from run to run and is too large given the nominal purity of our samples [6], to arise from foreign impurities. For two runs on the $x \sim 0.27$ sample we found $\Delta T_c \propto n_\gamma$, supporting this interpretation of ΔT_c. It should be clear from figure 1 that the thermodynamic instability overwhelms these extrinsic effects ; the existence of an accessible critical point in $Ce_{1-x}Th_x$ provides a unique opportunity to address certain questions, which can be readily resolved within these limitations.

Figure 3*a* shows that χT is linear out to ~ 50 K ; i. e., $\chi(T) = \chi(0) + B/T$. In figure 2 we have substract-

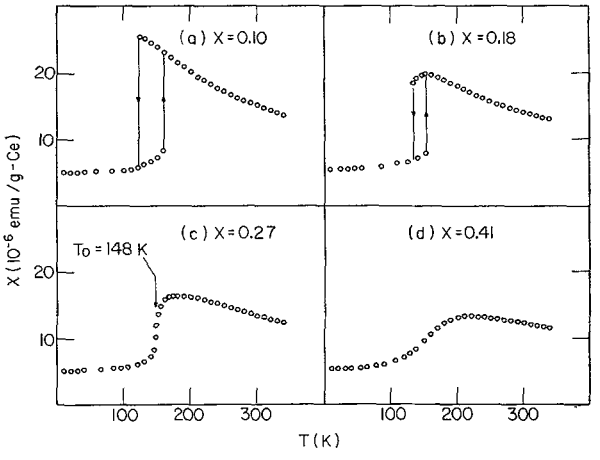

FIG. 2. — Magnetic susceptibility of $Ce_{1-x}Th_x$ for four concentrations x bracketing x_0.

ed B/T, as well as a thorium contribution (0.4×10^{-6} emu/g-Th). The values of $\chi(0)$ are plotted against x in figure 3*b*. They do not reproduce, but figure 3*c* indicates they are linear in n_γ, extrapolating at $n_\gamma = 0$ to the value of ref. [7] where great precautions were taken to ensure complete transformation. It is as though for the α-state :

$$\chi(T) = \chi^{\text{corr}}(0) + n_\gamma\,[288 + (5\,760/T)]\ 10^{-6} \text{ emu/g-Ce}.$$

The corrected values are plotted in figure 3*d* ; they are constant at 3.75×10^{-6} emu/g-Ce out to $x = 0.27$. In figure 4 we plot the γ-state data ; the solid lines represent $C/(T + \theta)$ behaviour with $C = 6\,000 \times 10^{-6}$ emu-K/g-Ce ; $\theta(x)$ is shown in the inset. Plotting

$$T^*(T) = \Delta(\chi T)/[\mathrm{d}(\chi T)/\mathrm{d}T]$$

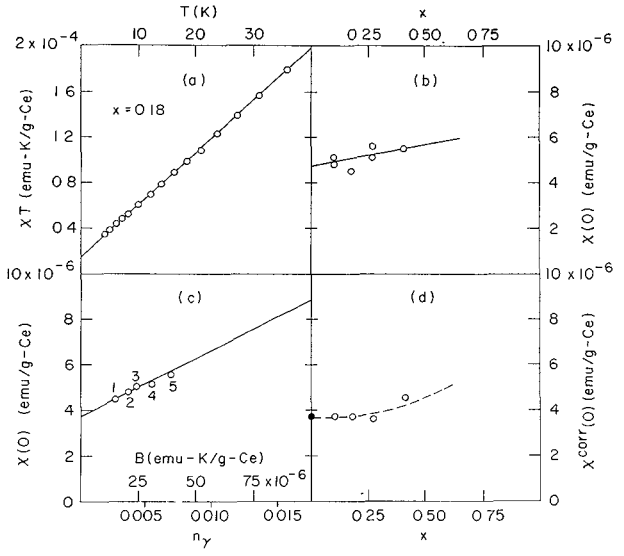

FIG. 3. — (*a*) χT vs. T for $x = 0.18$, demonstrating that $\chi(T) = \chi(0) + B/T$, (*b*) $\chi(0)$ as determined in (*a*) plotted vs. x, (*c*) $\chi(0)$ plotted vs. B. Point 1, $x = 0.18$; 2, $3\ x = 0.10$; 4, $5\ x = 0.27$. The solid line represents $\chi(0) = \chi^{corr}(0) + 288\ n_\gamma$ (see text), (*d*) values of $\chi^{corr}(0)$ vs. x. The $x = 0$ point is from ref. [7].

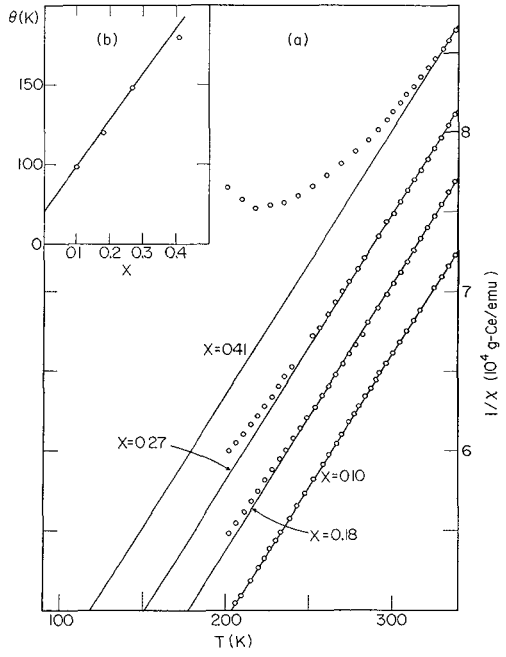

FIG. 4. — $1/\chi$ vs. T in the γ state for the four samples of figure 2. The solid lines represent $C/(T + \theta)$ behaviour where $C = 6\,000$ emu-K/g-Ce and the values of $\theta(x)$ are shown in the inset.

in figure 5 we see that χT couples linearly to the order parameter near (x_0, T_0). The solid lines in the inset are consistent with an equation of state, with $\Delta\rho$ replaced by $\Delta(\chi T)$, having $A = 118$ K, $B = 150$ K. Since no effort was made to account for non-critical background in χT, we think this is quite encouraging

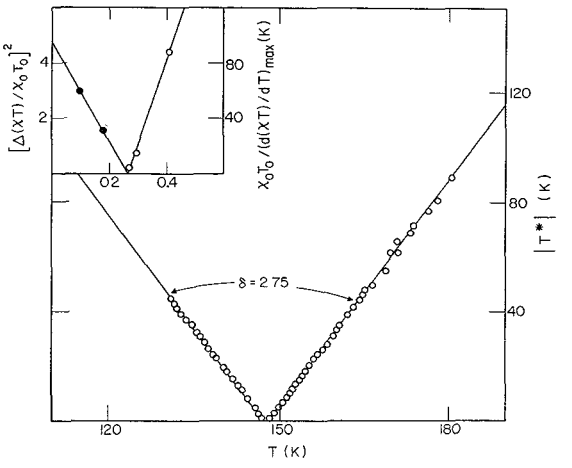

FIG. 5. — Inset : Squared first order jumps and inverse maximum derivatives for χT, vs. concentration. Main curve : $|\ T^*(T)\ |$ (see text) for a nearly critical sample. That the exponent $\delta = 2.75$ is essentially the mean field value demonstrates the linear coupling of χT to the order parameter.

agreement with the parameters obtained from resistivity.

3. **Discussion.** — The mean field equation of state is seen to represent the data by 5-10 % in the critical region. Intrinsic deviations arise from higher order terms in the Landau expansion and breakdown of the linear coupling of $\Delta\rho$ to Δn_f (which presumably is the microscopic order parameter). When the coupling is valid we can substitute Δn_f for $\Delta\rho$, and integrate eq. (1) to obtain the free energy :

$$F = \sigma \left\{ \frac{A}{4} \left(\frac{\Delta n_f}{n_0}\right)^4 + \frac{B}{2} \left(\frac{\Delta x}{x_0}\right) \left(\frac{\Delta n_f}{n_0}\right)^2 + \right.$$
$$\left. + \left[D \left(\frac{\Delta x}{x_0}\right) - \Delta T \right] \left(\frac{\Delta n_f}{n_0}\right) \right\}. \qquad (2)$$

We have discussed the meaning of each term in refs. [4] and [5] ; here we offer several comments. The 4f spin entropy, reflected in the $-\Delta T\,\Delta n_f$ term, is an important factor in stabilizing integral valence. Thus any mechanism (e. g., crystal fields) which removes magnetic entropy will make delocalization more favorable. The slope of the phase boundary $(\Delta T/\Delta x = D/x_0)$ (which is expected to depend on solute size, since this gives rise to an effective PV term in eq. (2)) has been found [5] to depend on solute size and valence independently ; in particular, the effect of thorium dilution is to strongly increase $\Delta T/\Delta x$ relative to the effect of a trivalent solute of the same size. Charge transfer from tetravalent cells to trivalent cells would increase the screening of the 4f electron, promoting delocalization (and further screening) ; solutes of high (low) valence would then increase (decrease) T_c. We are suggesting that an electronic mechanism is operative in the valence transition ; indeed the data is

consistent with the Ramirez-Falicov [8] screening mechanism, as extended to alloys by Alascio *et al.* [9].

The non-linear interaction driving the valence transition represented by the $\Delta x(\Delta n_f)^2$ term, must tend to change sign at $x = x_0$. To give rise to meanfield behaviour it must also involve a long force range [3]. Utilizing the Ginzburg criterion, the equation of state parameters and region of fit, we have obtained [6] a lower limit of $\zeta(x = 0\ ;\ T = 0) > 7$ Å. Any purely electronic mechanism would be screened out over ~ 2 Å ; hence, a lattice-mediated interaction must be involved. In one proposal [10] the lattice collapse on delocalization lowers the s, d band bottom, moving E_f yet closer to ε_F, promoting further delocalization. However, as an opposing tendency, the bandwidth also increases. This treatment correctly gives that the interaction becomes less attractive with increasing x or P ; but it requires insertion of a phenomenological negative interaction parameter to give first-order transitions. In a second treatment [11] pure cerium is treated as a pseudo-binary alloy of tri- and tetra-valent atoms, with 15 % size mismatch ; phase segregation occurs due to an infinite ranged attractive interaction between ions of identical size. This would give rise to first-order transitions and mean-field theory. However, since the intermediate valence state involves hybridized wave functions all atoms are identical over any longer time scale than $\tau_{VF} \sim h/\Gamma$, and the force range for a size mismatch interaction is cut off at roughly $\tau_{VF}\, v_s$ where v_s is the velocity of sound. For cerium, taking $\Gamma/k = 150$-$1\,500$ K (see below), this would be 0.7-7 Å. It is indeed unfortunate that extrinsic effects prevent us from measuring any closer to $(x_0,\ T_0)$ to see whether mean field theory begins to break down. A plausible picture is that an electron screening mechanism provides the fundamental negative interaction and that the lattice couples to pressure or alloying strains in such a way as to drive the transition second-order and dominate the critical behaviour.

To begin the discussion of the susceptibility we first consider crystal field effects. In a cubic environment the cerium $J = 5/2$ moment has a doublet lowest with a quartet raised by an energy Δ, which in cerium intermetallics is typically 50-100 K. At $T = 0$ the moment is reduced by 5/21 ; however χT saturates very rapidly above $T \sim \Delta/k$ [12]. We estimate [6] that the γ-state Curie-Weiss dependence cannot reflect crystal fields unless $\Delta \gtrsim 700$ K, which is extremely unlikely. In the intermediate valence state if Δ is not too much smaller than Γ then crystal fields may be important, due to the low temperatures and the lattice collapse.

As seen in figure 2 the α state susceptibility is temperature independent below 50 K, consistent with the fermi liquid picture discussed above [2]. If $\chi(0) = C/\Gamma$ then $\Gamma \sim 1\,500$ K ; however, a hybridization gap [2], paramagnon enhancement of $\chi(0)$, or crystal field reduction of the moment all would cause the value of Γ estimated in this simple fashion to be considerably in error. The upturns in χ above 50 K, first noted in ref. [7], could reflect crystal fields and/or inherent fermi liquid behaviour, as well as precursive transition effects.

The quantity $\chi^{corr}(0)$ shows only weak variation with alloying (Fig. 3*d*), while the γ-state Curie-Weiss parameters vary strongly with x (Fig. 4*b*). θ roughly tracks the limit of stability of the γ state, defined as the first order cooling transition temperature $T_c^-(x)$ Curie-Weiss behaviour is, of course, extremely common, given a limited region of data ; the fact that $\theta(x) \approx T_c^-(x)$ gives at least some support to our intuitive feeling that these parameters reflect fundamental energetics.

Phenomenologically [13] one expects

$$\chi = Cn_f/(T + T_{VF})$$

where $kT_{VF} \sim h/\tau_{VF}$. Thus the Curie-Weiss behaviour observed in the γ state might indicate an incipient valence fluctuation. However, the observed Curie constant is essentially that of the free $J = 5/2$ ion (with 4 % enhancement due perhaps to polarization of the s, d band electrons by the 4f moments) which together with the lattice constant suggests total occupancy. Alternatively we have proposed [5] that such behaviour might be due to a spin fluctuation-distinct from a valence fluctuation in not being volume-coupled. When E_f is close to ε_F then $\Delta\varepsilon$ enters the 4f-s, d exchange parameter J_{sf} as an energy denominator. The large temperature independent resistivity and giant thermopower observed in γ-cerium would then arise from spin scattering with

$$\rho \sim J_{sf}^2\, N n_f\, S(S + 1)\,.$$

If one could stabilize γ-cerium to $T = 0$ one might expect to observe a resistance minimum and thermopower maximum as observed in trivalent cerium intermetallics (e. g. $CeAl_3$) ; the valence transition, however, occurs at a higher temperature. The spin fluctuations should have an important effect on the susceptibility. However, in a concentrated system the large J_{sf} responsible for the spin fluctuation also leads to an enhanced 4f-4f RKKY exchange $\theta_{RKKY} \sim J_{sf}^2$ (1). While extrapolation from the other rare earths suggests $\theta(x)$ is two orders of magnitude too large to reflect ordinary exchange, it is plausible that the observed $\theta(x)$ values represent such enhanced RKKY exchange. Given the present status of Kondoesque theory for concentrated systems, it is not possible to decide whether the Curie-Weiss law arises from indirect exchange between the cerium atoms or simply from spin fluctuations. In either case the variation of $\theta(x)$ on alloying would be consistent with the mechanism whereby charge transfer from the tetravalent solute promotes smaller $\Delta\varepsilon$, hence larger J_{sf}.

By phenomenology ($\chi = Cn_f/(T + T_{VF})$) one would

(1) Varma, C. M., private communication.

expect $\chi(T + \theta)$ to couple linearly to n_f near T_0. Attempts to fit to such expressions fail badly ; rather, as seen from figure 5, χT couples linearly to the order parameter. It is also of interest to compare the regions of linear coupling, which for χT is

$$[T_0 - 40\ \text{K},\quad T_0 + 40\ \text{K}]$$

but for ρ is $[T_0 - 40\ \text{K},\quad T_0 + 10\ \text{K}]$. If the large γ-state resistivity were due to spin scattering with $\rho \sim n_f J_{sf}^2 S(S + 1)$ we would expect good linear coupling where the spin is best established- i. e., for $T > T_0$. The breakdown above T_0 indicates either that J_{sf} varies rapidly (but non-critically) or that some other scattering mechanism is at work. We feel that the critical behaviour of χT and ρ warrant theoretical examination.

4. **Conclusion.** — From a variety of physical measurements we have constructed a quantitative equation-of-state of the Landau meanfield form, which describes well the valence transition in $Ce_{1-x}Th_x$ and provides clues to the nature of the driving mechanism for the transition. The fact that the integral valence state is paramagnetic leads to rich complexities in the regime $T \gtrsim T_0$, owing to the possibly comparable importance of Kondo-like fluctuations, valence fluctuations and precursive magnetic ordering effects. For $T \ll T_0$, the system settles into a non-magnetic many-body ground state which exhibits Fermi-liquid behaviour. It is hoped that inelastic neutron scattering experiments now in progress will resolve some of the questions generated by the present study, in particular, the magnetic behaviour for $T \gtrsim T_0$.

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