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P-T-H phase diagram of heavy-electron UCd_{11}

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At ambient pressure UCd_{11} undergoes a phase transition near 5 K that is believed to arise from antiferromagnetic order within a strongly correlated electron system. Under moderate hydrostatic pressures, two new phase transitions appear below 5 K that are manifested by anomalies in the temperature-dependent electrical resistivity. We present the evolution of these transitions with pressure, temperature, and magnetic field and discuss possible interpretations of their origin given the pressure dependence of the resistivity and magnetic susceptibility.

INTRODUCTION

The observation that superconductivity can appear within a system of strongly correlated electrons having huge effective electronic masses has stimulated the search for additional examples of heavy-electron behavior.[1] Such searches have led to the discovery[2–4] of two uranium-based heavy-electron materials that order magnetically at low temperatures. Characteristic of the strong electronic correlations in each of these is a very large value of the electronic specific-heat parameter γ. Of the two [U_2Zn_{17} (Ref. 2) and UCd_{11} (Ref. 3)], UCd_{11} has the largest γ value, 840 mJ/mole K^2, obtained by extrapolating C/T versus T^2 from above the phase transition to $T=0$ K. Clear evidence[3] for a phase transition in UCd_{11} comes from a large peak both in the specific-heat and thermal-expansion coefficient at 5.05 K, as well as from a sharp drop in the electrical resistivity at the same temperature. Both the specific-heat and thermal-expansion anomalies are of a magnitude comparable to those observed[2] in U_2Zn_{17}, the ordering in which recently has been established by neutron diffraction to be antiferromagnetic with a much reduced ordered moment and a simple ordered structure.[5] However, the precise nature of the phase transition in UCd_{11} is considerably less well understood; although, muon spin rotation experiments[6] indicate antiferromagnetic order. Unlike the sharply defined phase transition in U_2Zn_{17}, the specific-heat C and thermal-expansion features near 5 K in UCd_{11} are characterized by rather broad high-temperature "tails" and a shoulder in C/T versus T^2 near 3.5 K. Because the U-U nearest neighbors are well separated (6.56 Å) in UCd_{11}, it might be expected that the uranium ions carry well-defined $5f$-electron moments. The large γ value, however, indicates the formation of a narrow band by hybridization.[3] In analogy with the speculation[1] that superconductivity in heavy-electron materials is of an unusual type, the nature of magnetic ordering in comparable systems may be similarly atypical in comparison with conventional f-electron magnetic systems.

By viewing the heavy-electron system in UCd_{11} as a Fermi liquid with a large effective mass of the quasiparticles, it is possible from the electronic specific-heat coefficient to estimate a corresponding characteristic degeneracy temperature T^* to be on the order of 10 K.[7] Therefore, the phase-transition temperature and T^* are of comparable magnitudes. Given this observation, one expects the phase transition to be sensitive to slight perturbations of the electronic system, such as can be accomplished by the application of moderate hydrostatic pressures. With this in mind, we have studied the temperature-dependent electrical resistance and magnetic susceptibility of UCd_{11} subjected to hydrostatic pressures exceeding 17 kbar and 7 kbar, respectively.

EXPERIMENTAL DETAILS

The electrical resistance was measured using a standard four-lead ac technique from room temperature to typically 1.3 K. Experiments were performed on a small single crystal of UCd_{11} which was grown from excess molten cadmium. X-ray analysis performed on crystals grown at the same time as the one employed in this work confirmed the cubic $BaHg_{11}$ crystal structure and gave a lattice parameter of 9.283 Å. There was no evidence from the x-ray study for the presence of second phases. Hydrostatic pressures were produced in a self-clamping Be-Cu pressure cell, with a mixture of 1:1 isoamyl alcohol and n pentane as the pressure-transmitting medium. Pressures within the cell were determined at low temperature from the inductively measured superconducting transition of lead. These measurements provide a relative accuracy in pressure determinations of better than ± 0.5 kbar. Additional details of the pressure cell and measurement procedures have been given elsewhere.[8]

A similar, though significantly miniaturized, pressure cell made of binary beryllium-copper was used for susceptibility χ measurements in a Faraday magnetometer. The susceptibility of UCd_{11} single crystals from the same batch as the resistivity sample was determined by subtracting the susceptibility of the empty cell from that of the cell containing crystals. In order to minimize systematic errors associated with measurements near $\chi=0$, the diamagnetism of beryllium-copper was compensated by wrapping Pt foil around the cell body. All measurements were performed in a dc field of 1 T and in the temperature range $2<T<300$ K for pressures up to 7.6 kbar.

RESULTS

In Fig. 1 we show the electrical resistance of UCd_{11} at four different pressures. The detailed shape of the zero-pressure curve agrees with that published[3] previously, including a distinct break in the curve at 5.04 K (see Fig. 1 inset) that signals the phase transition. With increasing pressure the broad resistance maximum centered at $T_{max}=84$ K (for $P=0$) shifts approximately linearly to lower temperatures at a rate of -1.6 K/kbar and becomes more prominent. We also observe in Fig. 1 a rather large, systematic increase in the overall resistance with applied pressure. Near room temperature the resistance increases linearly with pressure at the relative rate $(1/R_0)dR/dP \simeq 0.01$/kbar. Although we cannot disregard the possibility that the resistance rise might be due to the formation of microcracks, we note that the measurements were performed on a single crystal and that, after an initial pressure increment, there was no detectable hysteresis in the room temperature resistance with repeated pressure cycling.

The occurrence of a phase transition is observed most clearly in plots of the temperature derivative of the resistance $\partial R/\partial T$ versus temperature [see Fig. 2(a)]. In the vicinity of the phase transition, this curve appears similar to that of C_{el}/T versus T measured[3] at ambient pressure. With increasing pressure [Figs. 2(b) and 2(c)] there is a significant change in the temperature dependence of R below 4 K that culminates in the appearance of a new phase transition near 3 K at 2.8 kbar. Concurrent with the evolution of the new transition T_2 is a gradual shift of the original phase transition T_1 at temperature T_{1c} to

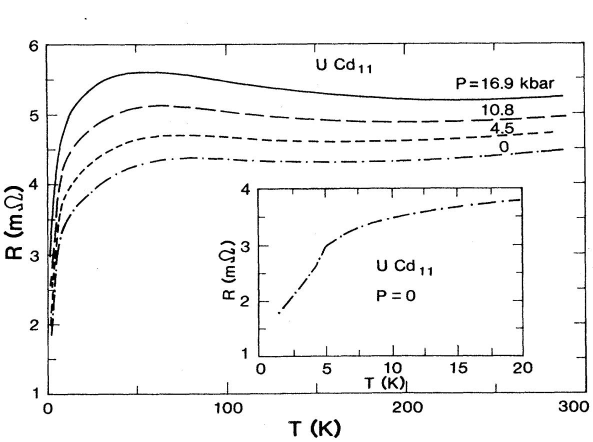

FIG. 1. The electrical resistance of single crystal UCd_{11} as a function of temperature at four pressures. We estimate the room temperature resistivity to be about 100 $\mu\Omega$-cm at $P=0$.

higher temperatures and a diminution of its $\partial R/\partial T$ signature, i.e., an apparent decrease in the spin-disorder scattering removed by the phase transition. (In the following we refer to phase transitions T_i which are defined by their respective pressure- and field-dependent critical temperatures T_{ic}.) T_{2c} falls rapidly toward $T=0$ K [Figs. 2(d)–2(f)] as the pressure is raised above ~ 5 kbar. At the highest pressures [Fig. 2(i)], a third transition T_3 appears whose signature is characterized by a negative-going peak in $\partial R/\partial T$. Both T_2 and T_3 are also clearly discernible in plots of R versus T.

Specific-heat measurements[3] at ambient pressure show that T_{1c} is depressed somewhat over 1 K by an 11 T magnetic field. We also have studied the influence of magnetic fields to 4 T on the transitions T_2 and T_3 at pressures of 3.8 and 17.3 kbar, respectively. These measurements were performed, with the pressure cell immersed in liquid helium, by fixing the magnetic field and slowly sweeping the temperature through the transition. Starting conditions for each measurement cycle were $T=4$ K, $H=0$ T. Both T_{2c} and T_{3c} were found to be nonlinear functions of H with T_{2c} (3.8 kbar) decreasing by nearly 1.5 K in 4 T and T_{3c} (17.3 kbar) increasing by over 0.5 K at 3 T. The *P-T-H* phase diagram for UCd_{11} resulting from these studies is shown in Fig. 3.

The dependence of T_{1c} on pressure is unusual, increasing initially at a rate of ~ 70 mK/kbar, reaching a plateau between 8 and 13 kbar, and finally increasing again at a rate of about 100 mK/kbar. The initial rate of increase in T_{1c} can be compared to that expected on the basis of Ehrenfest's equation[9] appropriate for second-order phase transitions

$$\partial T_{1c}/\partial P = 3VT_{1c}\Delta\alpha/\Delta c_p \ ,$$

where $\Delta\alpha$ and Δc_p are the thermal-expansion and specific-heat changes, respectively, at $T_{1c}(P=0)$ and V is the molar volume. From the measurements of Fisk *et al.*,[3] we estimate $\Delta\alpha \approx 20\times 10^{-7}$/K and $\Delta c_p \approx 8$ J/mole K, which give $\partial T_{1c}/\partial P \approx 60$ mK/kbar, a value in reasonable agreement with that determined directly.

A most striking feature in this work is the observation of two new phase transitions in UCd_{11} that are separated by only about 14 kbar. The *P-T-H* diagram suggests a possible inter-relationship between phases T_1 and T_2 as well as between T_1 and T_3. We see in Fig. 3 that T_2 disappears near the pressure where T_{1c} becomes independent of pressure and T_3 appears when T_{1c} once again depends on pressure. This correspondence is supported further by the systematics in the resistivity data of Fig. 2. At the same time it is clear from the sign difference in field derivatives of T_{2c} and T_{3c} that these transitions are quite different. There is some indication from specific-heat measurements[3] that perhaps the second transition is beginning to form already at ambient pressure. As mentioned earlier an unexplained shoulder occurs near 3.5 K in a plot of C/T versus T^2. This temperature agrees well with that obtained by smoothly extrapolating the phase boundary $T_{2c}(P)$ to $P=0$. Despite attempts to observe an unambiguous signature for the second transition at pressures less than 3 kbar, no evidence for T_2 could be

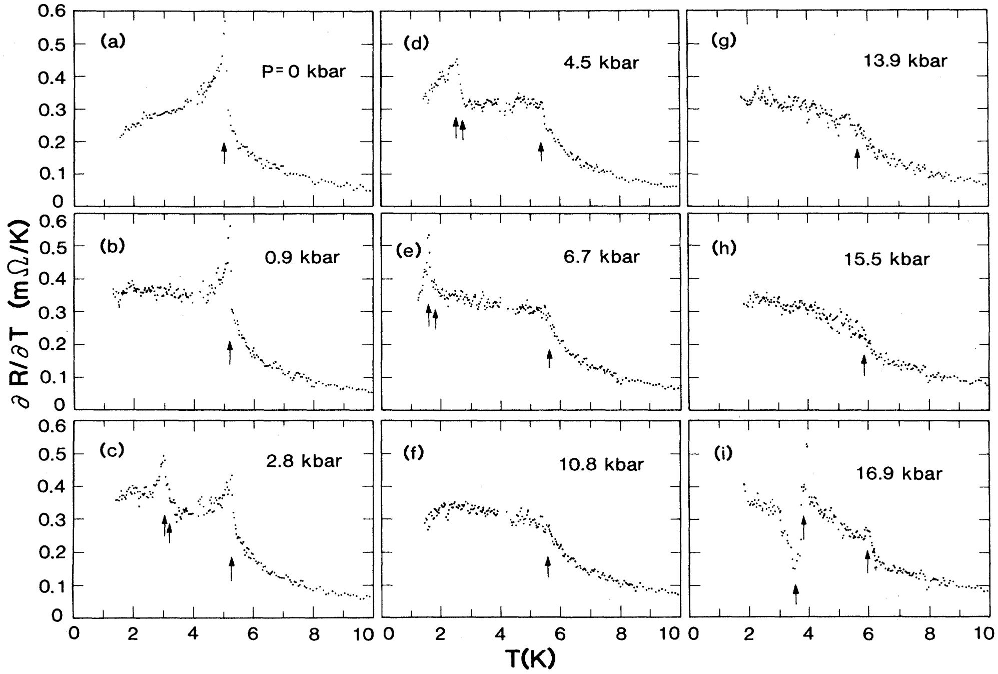

FIG. 2. Temperature derivative of the electrical resistance $\partial R/\partial T$ as a function of temperature at fixed pressures and zero-applied magnetic field. Arrows denote the temperature at which a phase transition appears. For transitions induced by pressure, two arrows are shown corresponding to different criteria applied to define the transition.

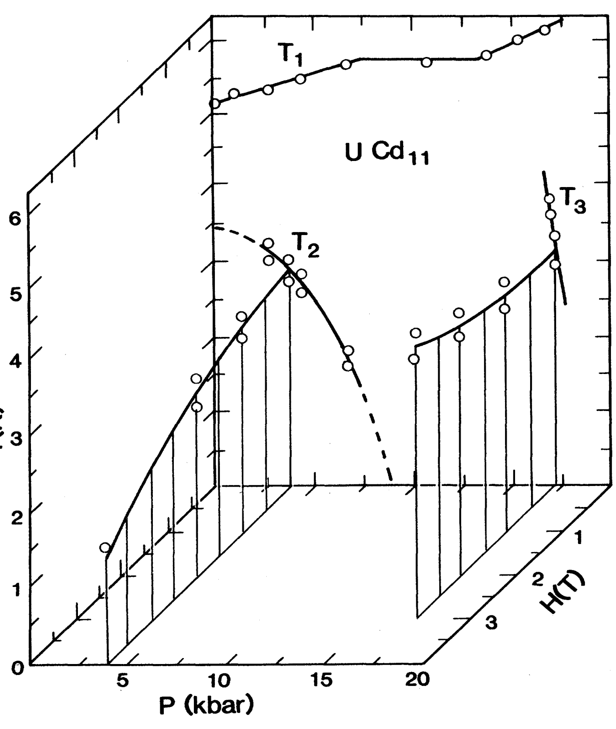

FIG. 3. The pressure-temperature-magnetic field phase diagram for UCd_{11}. Lines are guides to the eye. The set of two open circles used to define the transitions T_2 and T_3 correspond to different criteria signalling the transition (see Fig. 2).

found. However, as shown in Figs. 2 (a)–2(c), there is a systematic development in $\partial R/\partial T$ leading up to the phase transition. This trend could be interpreted as arising from an increase in magnetic scattering at temperatures less than $T_{1c}(P)$, corresponding to a progressive decrease in spin-spin correlations[10] below T_{1c} as pressure is applied.

Figure 4 shows the temperature dependence of the inverse molar susceptibility of UCd_{11} at the two extremes

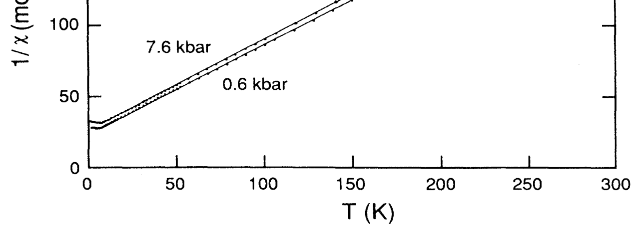

FIG. 4. Inverse magnetic susceptibility as a function of temperature for UCd_{11} subjected to pressures of 0.6 and 7.6 kbar. The inset shows the effect of pressure on the magnetic susceptibility in the vicinity of the phase transition T_1.

of our pressure measurements. Slopes of these curves give effective moments μ_{eff} of 3.60 ± 0.02 and 3.57 ± 0.02 μ_B/U for $P=0.6$ and 7.6 kbar, respectively, values consistent with either $5f^2$ or $5f^3$ configurations at both pressures. The intercepts provide negative paramagnetic Curie temperatures whose magnitudes increase with pressure from 39.4 ± 0.3 to 41.7 ± 0.3 K. Although it is difficult to determine from these measurements the precise pressure dependence of T_{1c}, a clearly positive trend is observed, as displayed in the inset of Fig. 4. Because of the limited temperature range over which these measurements could be made and the fact that a 1 T field was applied to the sample, no distinct evidence for phase transition T_2 could be detected. However, the systematic change in the temperature dependence of χ below T_{1c} might hint of a pressure-induced suppression of T_{2c}. We also note a progressive broadening of the susceptibility maximum near T_{1c} that is consistent with the trends in $\partial R/\partial T$ shown in Figs. 2(a)–2(e).

DISCUSSION

As mentioned, muon spin-rotation and relaxation experiments[6] indicate that the phase transition T_1 is due to antiferromagnetic order. This has not yet been confirmed by neutron scattering but only an upper limit of $1.5\mu_B$/U on the ordered moment has been established.[11] Such a reduced ordered moment is consistent with neutron measurements on related systems U_2Zn_{17} (Ref. 5) and UCu_5 (Ref. 12) and with the ratio of the electronic specific-heat contributions above and below the Néel temperature.[11] That the ordered moment is significantly less than μ_{eff} inferred from susceptibility measurements at temperatures higher than T_{1c} suggests[5] the presence of Kondo-like interactions leading to partial compensation of the local moment at reduced temperatures. Such interactions, together with Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions, also appear important for determining the temperature dependence of transport and magnetic properties.[1]

Many Ce- and U-based heavy-electron compounds have a maximum in their electrical resistivity at some moderately low temperature T_{max}, as is also the case in UCd_{11} (Fig. 1). Pressure measurements[13] show that, unlike UCd_{11}, in almost all of these cases $dT_{max}/dP>0$; however, for Yb-based systems with a low-temperature resistivity maximum, $dT_{max}/dP<0$.[14] This behavior also has been attributed to the pressure-dependent competition between intrasite Kondo-like interactions and intersite RKKY-type interactions.[13,14] Presumably in most Ce- and U-based compounds, pressure ostensibly favors a less-magnetic ground state due to the relatively more rapid increase in Kondo spin compensation than the enhancement of RKKY interactions. The heavy-electron superconductor UBe_{13}, however, appears to provide[13] a case in which a more-magnetic-like ground state is favored by pressure even though $dT_{max}/dP>0$. On the other hand, in Yb systems, the low volume state is more magnetic and hence generally promoted by applied pressure.

A different example of the behavior described is found in $CeAl_2$ in which the resistivity maximum near 100 K moves to lower temperatures with increasing pressure.[15] Here, however, T_{max} has been attributed to Kondo-like scattering off thermally populated crystalline-electric field levels whose splitting from the ground state decreases with pressure. Although the presence of crystal fields has been established in a number of Ce compounds, including $CeAl_2$,[15] this is not true of U compounds, with the exception of UPd_3.[16] The $1/\chi$ versus T data shown in Fig. 4 would suggest that crystal fields are not well-defined and certainly not manifested clearly in UCd_{11}. Even in the absence of crystal-field splittings, we would expect to find an entropy of $R\ln2$ below T_{1c} in UCd_{11}, characteristic of the strongly interacting Fermi liquid ground state inferred from the large γ value. Our analysis of the specific heat data[3] for UCd_{11} up to T_{1c} does give an entropy slightly less than $R\ln2$ consistent with this expectation. It is also not obvious that pressure effects in UCd_{11} and Yb compounds ($dT_{max}/dP<0$) can be interpreted similarly. This is made particularly difficult because the two possible $5f$ configurations have nearly identical effective moments.

UCd_{11}, therefore, appears to be somewhat pathological in the sense that it is not straightforwardly analogous to previously studied systems. However, we believe that our observations are generally consistent with the concept of competing intra- and intersite interactions. In this perspective, the large electronic specific-heat coefficient γ is determined primarily by the intrasite energy scale T_K.[7] For $T_K \gtrsim T_R$, where T_R is a measure of the intersite coupling scale determined by the q-dependent exchange J, the ground state is paramagnetic. However, when $J(q)/T_K=1$ a magnetic instability occurs and the spin-system orders.[17] Because UCd_{11} has the largest γ of any known U-based heavy-electron magnet, this viewpoint suggests that T_K must be small, certainly smaller than T_R. In this regime we expect the magnetic ground state to be favored initially as J is enhanced by pressure,[18] producing $\partial T_{1c}/\partial P>0$. At much higher pressures, when T_K and T_R become comparable, Kondo spin compensation dominates and we would expect $\partial T_{1c}/\partial P<0$. Evidence[19] for this trend is found from pressure measurements of the Neel temperature T_N in U_2Zn_{17} in which T_R and T_K have been argued to be more comparable. Again because of the large ratio T_R/T_K in UCd_{11}, RKKY interactions will dominate with initial increments in pressure, producing $dT_{max}/dP<0$ even though the ratio T_R/T_K becomes smaller. (For simplicity this argument ignores q-dependent effects which may be important. See below.) Similar arguments can be used to predict the behavior of Yb-based heavy-electron materials under pressure. Although the point of view developed here would suggest that at sufficiently high pressures dT_{max}/dP should reverse sign, as well as $\partial T_{1c}/\partial P$, in UCd_{11}, for Yb systems this should not occur within a comparable pressure range since the low volume, magnetic state will always be favored. Such a distinction could be tested straightforwardly.

This simple picture is also consistent with the pressure dependence of the susceptibility. The dc magnetic susceptibility detects the $q \rightarrow 0$ limit of the generalized susceptibility measured in quasi-elastic scattering. At low temperatures $\chi \sim 1/\Theta$, where Θ is the paramagnetic Curie temperature, which for a single Kondo impurity system is proportional to T_K. However, in the case of a lattice of Kondo impurities, Θ is not so simply described because of the existence of intersite correlations. Unfortunately, no simple expression for Θ exists in this case; however, the data of Fig. 4 indicate $d|\Theta|/dP > 0$, consistent with the expected increase in T_K with pressure. If we assume that spectral weight lost at $q \simeq 0$ by the application of pressure reappears at some $q > 0$, then a second magnetic instability $[J(q)/T_K = 1]$ could occur. We suggest that this may be the mechanism responsible for the additional phase transition T_2. Its extremely strong suppression with pressure, however, is not understood.

As mentioned above, the phase diagram presented in Fig. 3 clearly suggests an inter-relationship between phase transitions T_1 and T_2 as well as T_1 and T_3. Although a plausible argument has been given for the origin of T_2 and the pressure dependence of T_1 at low pressures, the source of T_3 remains a mystery. Certainly additional experiments, e.g. specific heat, magnetic susceptibility at higher pressures and lower temperatures, as well as neutron scattering under pressure, are required to clarify our understanding of the most interesting *P-T-H* behavior of UCd_{11}.

SUMMARY

Electrical-resistivity and magnetic-susceptibility measurements on UCd_{11} as functions of pressure reveal two new phase transitions that are both strongly volume dependent and couple to an applied magnetic field. The pressure dependences of T_{1c} and T_{max}, as well as the large electronic specific heat coefficient and reduced ordered moment of UCd_{11}, are consistent with the competition between intersite (RKKY-like) and intrasite (Kondo-like) interactions in which at low pressures intersite interactions dominate. We suggest that the phase transition first induced by pressure (T_2) arises from a volume-dependent change in the q-dependent susceptibility. At present, no explanation exists for the source of the second pressure-induced transition (T_3) except to note that it appears to be coupled to the magnetic transition T_1, which itself may have been modified in a subtle way by pressure sufficiently large to give T_3.

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[1]For experimental reviews of heavy-electron behavior see H. R. Ott and Z. Fisk, in *Handbook on the Physics and Chemistry of the Actinides,* edited by A. J. Freeman and G. H. Lander (Elsevier, Amsterdam, 1987), p. 85; Z. Fisk, D. W. Hess, C. J. Pethick, D. Pines, J. L. Smith, J. D. Thompson, and J. O. Willis, Science **239**, 33 (1988).

[2]H. R. Ott, H. Rudigier, P. Delsing, and Z. Fisk, Phys. Rev. Lett. **52**, 1551 (1984).

[3]Z. Fisk, G. R. Stewart, J. O. Willis, H. R. Ott, and F. Hulliger, Phys. Rev. B **30**, 6360 (1984).

[4]Two other U-based compounds, UCu_5 and $UAgCu_4$, order magnetically and may be considered to belong to the class of heavy-electron compounds but their γ is less than 400 mJ/mole K^2. See Ott and Fisk (Ref. 1) for additional details.

[5]C. Broholm, J. K. Kjems, G. Aeppli, Z. Fisk, J. L. Smith, S. M. Shapiro, and G. Shirane, Phys. Rev. Lett. **58**, 917 (1987).

[6]S. Barth, H. R. Ott, F. Hulliger, F. N. Gygax, A. Schenck, and T. M. Rice, Hyperfine Inter. **31**, 403 (1986).

[7]Z. Fisk, J. D. Thompson, and H. R. Ott, J. Magn. Magn. Mater. (to be published).

[8]J. D. Thompson, Rev. Sci. Instrum. **55**, 231 (1984); D. Wohlleben and M. B. Maple, Rev. Sci. Instrum. **42**, 1573 (1971).

[9]See, for example, L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading. 1969), p. 181.

[10]M. E. Fisher and J. S. Langer, Phys. Rev. Lett. **20**, 665 (1968).

[11]J. D. Thompson, A. C. Lawson, M. W. McElfresh, A. P. Sattelberger, and Z. Fisk, J. Magn. Magn. Mater. (to be published).

[12]A. Murasik, S. Ligenza, and A. Zygmunt, Phys. Status Solidi (A) **23**, K163 (1974).

[13]J. D. Thompson, J. Magn. Magn. Mater. **63&64**, 358 (1987).

[14]J. D. Thompson, H. A. Borges, Z. Fisk, S. Horn, R. D. Parks, and G. L. Wells, in *Theoretical and Experimental Aspects of Valence Fluctuations and Heavy Fermions,* edited by L. C. Gupta and S. K. Malik (Plenum, New York, 1987), p. 151.

[15]M. Nicolas-Francillon, A. Percheron, J. C. Aachard, O. Gorochov, B. Cornut, D. Jerome, and B. Coqblin, Solid State Commun. **11**, 845 (1972).

[16]N. Shamir, M. Melamud, H. Shaked, and M. Weger, Physica **94b**, 225 (1978).

[17]G. Aeppli, in Ref. 14, p. 279.

[18]S. Doniach, in *Valence Instabilities and Related Narrow-Band Behavior,* edited by R. D. Parks (Plenum, New York, 1977), p. 169.

[19]J. D. Thompson, Z. Fisk, and H. R. Ott, J. Magn. Magn. Mater. **54-57**, 393 (1986).