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New heavy-fermion system, $NpBe_{13}$, with a comparison to UBe_{13} and $PuBe_{13}$

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We have prepared single crystals of $NpBe_{13}$, $Np_{0.68}U_{0.32}Be_{13}$, and $PuBe_{13}$ and measured their resistivity, susceptibility, and specific heat down to low temperatures. $NpBe_{13}$ has an itinerant-electron magnetic transition at 3.4 K, with a large temperature-dependent specific heat above this transition that is quite similar to that observed in the heavy-fermion superconductor UBe_{13} and a $\gamma(T=0)$ of approximately 900 mJ/mole K^2. $PuBe_{13}$ may be described as a Kondo-type system, with certain inconsistencies. The data are compared to results for UBe_{13} and are consistent with a narrow f band at the Fermi energy in UBe_{13} moving lower in energy with the addition of f electrons in heavier actinide elements to create a Kondo resonance by $PuBe_{13}$.

INTRODUCTION

Superconductivity was first reported in $CeCu_2Si_2$ in 1978 by Franz *et al.*, but ascribed to a second phase.[1] Steglich *et al.* reported[2] later on bulk superconductivity in $CeCu_2Si_2$ at 0.5 K, with the electronic specific heat γ ($C=\gamma T+\beta T^3$) of 1000 mJ/mole K^2 and sizable specific-heat jump, ΔC, at T_c indicating that extremely-heavy-mass (m^*) electrons were responsible for the superconductivity. Although the same large increase in γ (and m^*) as observed in $CeCu_2Si_2$ below 10 K had also been seen[3] in $CeAl_3$, no superconductivity was observed. Thus, the discovery of Steglich *et al.* marked a radical departure from all previous superconductors and started intense study of $CeCu_2Si_2$ and searches for other examples of "heavy-fermion" superconductivity. Bucher *et al.* reported[4] unusual superconductivity in UBe_{13} in 1975, but also ascribed the effect as due to second phase. In a collaboration between Eidgenössische Technische Hochschule Eurich and Los Alamos National Laboratory, this unusual superconductivity reported by Bucher *et al.* was recently found[5] by Ott *et al.* to be due to bulk superconductivity again with a large γ (1100 mJ/mole K^2) and sizable ΔC at $T_c=0.85$ K, i.e., a second example of heavy-fermion superconductivity. Recently, our group at Los Alamos has reported[6] bulk superconductivity in UPt_3, with a large m^* and low T_c (0.54 K), but with significant differences from $CeCu_2Si_2$ and UBe_{13}, including strong experimental evidence for the coexistence of spin fluctuations with the superconductivity in UPt_3.

A number of active materials investigations searching for more such systems are currently underway. We have prepared single crystals of $Np_{1-x}U_xBe_{13}$ ($0\leq \times \leq 1$) and $^{242}PuBe_{13}$ and characterized these compounds via resistivity, dc and ac magnetic susceptibility, and specific heat down to dilution refrigerator temperatures. The results revealed many insights about heavy-fermion systems.

SAMPLE PREPARATION

Samples were prepared by growth from a molten Al flux as in the preparation of UBe_{13} reported in Ref. 5. The ^{237}Np starting material had less than 100 ppm impurities, and various Pu isotopes whose sum was less than 0.1%. The half-life of ^{237}Np is 2×10^6 yr resulting in a self-heat (which affects the lowest attainable temperature of measurement) of approximately 0.073 mW/g. The isotope of Pu used was ^{242}Pu due to its factor of 13 lower self-heat (0.155 mW/g) than the next coldest isotope, ^{239}Pu. The isotopic purity of the ^{242}Pu is 99.91%, with less than 100 ppm other nongaseous impurities. Another reason for using ^{242}Pu despite its scarcity is that alpha emitters in contact with Be form intense neutron sources, with the neutron flux varying approximately inversely with the half-life. The radiation dose at contact with a 1-g charge of ^{239}Pu mixed with Be would, in fact, be uncomfortably high, approximately 4 R/h. The lattice constants a_0 measured on the resultant single crystals were 10.260, 10.267, and 10.294 Å for $Np_{0.68}U_{0.32}Be_{13}$, $NpBe_{13}$, and $PuBe_{13}$, respectively, compared to 10.254 Å for UBe_{13}.

RESULTS AND DISCUSSION

Alternating current susceptibility measurements on $U_{0.989}Np_{0.011}Be_{13}$ indicate a T_c of 0.62 K, a 0.3 K depression/percent Np. No superconductivity was detected in $Np_{0.68}U_{0.32}Be_{13}$, $NpBe_{13}$, and $PuBe_{13}$ down to 0.080, 0.080, and 0.4 K, respectively. Resistivity as a function of T, performed by a four-wire technique, for the latter three compounds plus UBe_{13} are shown in Fig. 1. It is interesting to note that the peak and shoulder structure observed in UBe_{13} are totally absent in $Np_{0.68}U_{0.32}Be_{13}$, and a peak of different shape appears to a small extent in $Np_{0.85}U_{0.15}Be_{13}$ (data not shown) and to a greater extent in pure $NpBe_{13}$. The resistance data for $PuBe_{13}$ show a broad peak at about 13 K.

The low-temperature dc magnetic susceptibility of MBe_{13}, where M = U, Np, and Pu has been measured by Brodsky and Friddle.[7] At higher temperatures they report a Curie-Weiss behavior for all three compounds, with effective moments of 2.99, 2.76, and 0.74 μ_B, respectively, roughly consistent with electronic configurations of $5f^3$ for UBe_{13}, $5f^4$ for $NpBe_{13}$, and $5f^5$ for $PuBe_{13}$. The χ-

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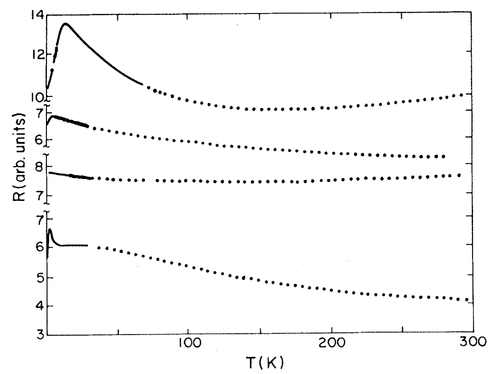

FIG. 1. Resistivity versus temperature for single crystals of UBe_{13} (lowest curve), $Np_{0.68}U_{0.32}Be_{13}$ (next curve up), $NpBe_{13}$ (third curve from the bottom), and $PuBe_{13}$ (top curve). The units for each curve are arbitrary; no intercomparison in absolute terms is possible between the four curves. The vertical axis does preserve the relative zero for each curve.

versus-T data for $PuBe_{13}$ are not monotonically increasing as for the other two compounds, instead going through a rather sharp peak (interpreted[7] as an antiferromagnetic transition) at 11.5 K, with $\chi_{max} \simeq 15 \times 10^{-3}$ emu/mole. Because the rather broad resistivity feature in our data for $PuBe_{13}$ and the structure in our resistivity data for $NpBe_{13}$

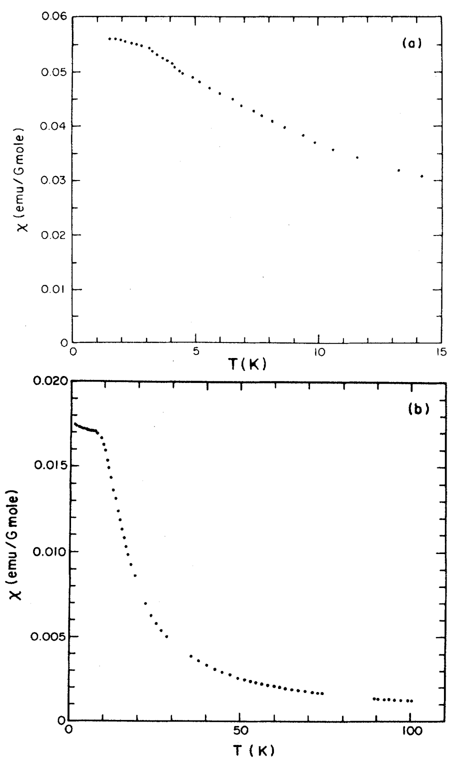

FIG. 2. (a) Magnetic susceptibility versus temperature for $NpBe_{13}$. Note the break in χ versus T just above 3 K. The χ of UBe_{13} is only about 0.015 emu/G mole at these temperatures. Thus, for χ/γ to be comparable in $NpBe_{13}$, γ for $NpBe_{13}$ would have to be over 3 J/mole K. (b) Magnetic susceptibility versus temperature for $PuBe_{13}$ with no peak at 11.5 K, in disagreement with Ref. 7.

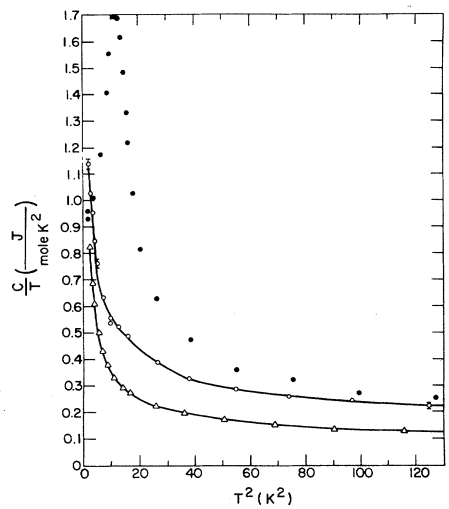

FIG. 3. Specific heat between 1.3 and 11 K for UBe_{13} (triangles), $Np_{0.68}U_{0.32}Be_{13}$ (open circles), and $NpBe_{13}$ (solid circles) showing clearly the increase of C/T as an additional f electron is added going from U to Np. The lines drawn are only to guide the eye.

seemed inconsistent with the susceptibility results of Brodsky and Friddle, as are our specific-heat data discussed below (i.e., their χ-versus-T data for $NpBe_{13}$ show no structure and their $PuBe_{13}$ susceptibility data showed too sharp a structure), we have measured the dc magnetic susceptibility of our $NpBe_{13}$ and $PuPe_{13}$ crystals. These data are shown in Fig. 2. For $NpBe_{13}$, our χ data show a slight break between 3 and 4 K, the same temperature where R-versus-T changes slope in Fig. 1, and are about 25% higher than in Ref. 7 at 2 K. For $PuBe_{13}$, our χ data show a rapid flattening out of χ-versus-T below about 10 K, reminiscent of Kondo behavior.[8] The unlikely possibility that the collection of single crystals of $PuBe_{13}$ which we measured were actually antiferromagnetic and had the spin axis aligned *perpendicular* to the applied field would also give the same shape of χ versus T as we observed. However, ac susceptibility showed no antiferromagnetic transition between 4 and 18 K.

The discrepancy between the χ data of Brodsky and

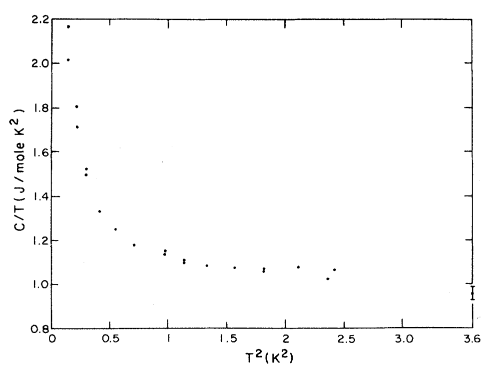

FIG. 4. Specific heat of $Np_{0.68}U_{0.32}Be_{13}$ between 0.38 and 1.9 K. The question of whether the sharp upturn at the lower temperatures is a magnetic transition is under further investigation.

Friddle and ours for $NpBe_{13}$ is easily explained—either our observation of a slight break is due to higher-quality samples in our single crystals or to the greatly improved temperature resolution of our data versus their ~2-K spacing between points. However, the large disagreement in our χ data and theirs for $PuBe_{13}$ seems irreconcilable. Even without our measurement of χ for $PuBe_{13}$, the resistivity and specific-heat data (discussed below) measured in this work argue strongly against antiferromagnetism in $PuBe_{13}$ around 11 K as claimed by Brodsky and Friddle.

Low-temperature specific-heat data between 1.3 and 11 K for UBe_{13}, $Np_{0.68}U_{0.32}Be_{13}$, and $NpBe_{13}$ are shown in Fig. 3. The large temperature dependence of γ below 10 K characteristic of $CeCu_2Si_2$ and UBe_{13} is seen in all the samples, with the magnitude of γ increasing with increasing Np content. For $NpBe_{13}$, a sharp transition at 3.4 K occurs, consistent with structure seen in the resistance and susceptibility data in Figs. 1 and 2. Below this transition, the C/T data fall back to an intercept γ of 0.9 J/mole K.[2] This is a significant decrease from the γ deduced from considering the scaling of the high-temperature data and the low-temperature γ values for UBe_{13} (1.1 J/mole K^2) and $Np_{0.68}U_{0.32}Be_{13}$ ($\gamma > 1.1$, see below). Considered with the slight change in χ at 3.4 K, this decrease in γ is consistent with some sort of itinerant magnetic transition. Using the specific-heat data for $Np_{0.68}U_{0.32}Be_{13}$ as an approximate background correction, the entropy associated with the specific-heat anomaly in $NpBe_{13}$ is approximately 40% of $R\ln 2$, also consistent with itinerant magnetism being the cause of the specific-heat, resistive, and susceptibility anomalies at 3.4 K.

The specific heat down to 0.4 K for $Np_{0.68}U_{0.32}Be_{13}$ is shown in Fig. 4. It is interesting to compare the relative temperature dependence of C/T for this material versus that for UBe_{13}. Above 3 K, the ratio

$$C/T\ (Np_{0.68}U_{0.32}Be_{13})/C/T(UBe_{13})$$

is approximately constant at 1.7 ± 0.15 (see Fig. 3). Below 3 K, the ratio starts to fall and around 1 K the specific heats for the two materials are approximately the same. This trend to a less rapid raise in C/T below 3 K for $Np_{0.68}U_{0.32}Be_{13}$ is clearly apparent in Fig. 4, where C/T, or γ, becomes almost constant down to 1 K. Then, below 1 K, C/T begins rising again for $Np_{0.68}U_{0.32}Be_{13}$, while UBe_{13} goes superconducting. This rapid rise may be either a further increase in the γ and the effective mass of the electrons due to stronger heavy-fermion behavior, or due to a magnetic transition similar to the one observed in $NpBe_{13}$ but occurring at lower temperatures.

The specific heat of $PuBe_{13}$ is shown in Fig. 5. The solid line drawn uses the lattice contribution determined from higher-temperature data from $Np_{0.68}U_{0.32}Be_{13}$, where the Debye temperature is 580 ± 30 K and a T^5 lattice contributions enters for $T>20$ K. This is consistent with the Θ_D determined[4] by Bucher *et al.* for $ThBe_{13}$ of 618 K. Although the solid line is only an approximate background for the electronic and lattice specific heat of $PuBe_{13}$ without the transition, subtracting this background from the measured data shows clearly in Fig. 6 that this anomaly resembles a Kondo peak.[8] The temperature dependence of the C data above the peak in Fig. 6 is approximately T^{-8}, definitely ruling out a Schottky peak (where $CXXT^{-2}$). Thus, the data as shown in Fig. 6 support our susceptibility results for $PuBe_{13}$.

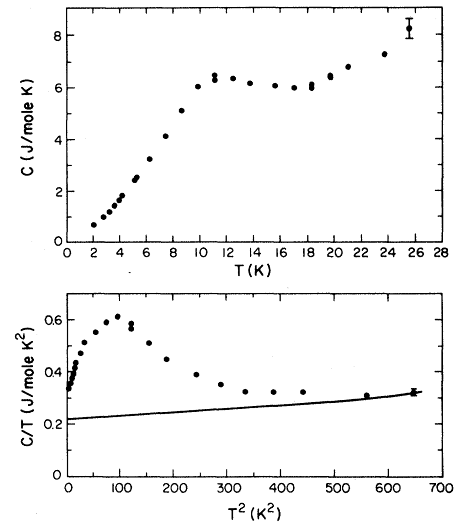

FIG. 5. Low-temperature specific heat of 10 mg of $^{242}PuBe_{13}$. The addenda correction rises to 50% at 25 K. Although data below 1.5 are needed to be certain, it appears that the low- and high-temperature γ's are approximately equal.

SUMMARY AND CONCLUSIONS

As an additional f electron is slowly added to UBe_{13} by substituting Np for the U, superconductivity is suppressed while the temperature-dependent heavy fermion γ remains all the way over to pure $NpBe_{13}$. Adding a further f electron by going on to Pu destroys the large temperature dependence γ. Furthermore, in going from UBe_{13} to $NpBe_{13}$ superconductivity is apparently replaced by some form of itinerant-electron magnetism. This itinerant-electron magnetism turns into Kondo-type behavior in $PuBe_{13}$. The occurrence of magnetic behavior in $NpBe_{13}$

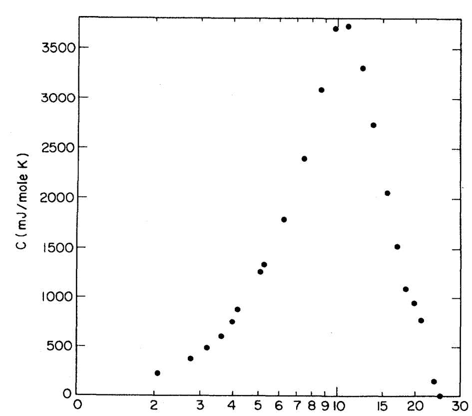

FIG. 6. Using the approximate extrapolation indicated by the solid line in Fig. 5, $C^{magentic}=C^{measured}-C^{extrap}$ is shown versus $\log T$ here. The shape is not unlike a Kondo peak (Ref. 8).

where the f electrons are so highly correlated is not surprising. What is interesting to note is that in the continuous change of properties in $Np_{1-x}U_xBe_{13}$, a quite large replacement of U by Np (at least over half) is required before this magnetic behavior is manifested, even though superconductivity is quite rapidly depressed. Thus, the heavy-fermion ground state with such highly correlated high-mass f electrons is not particularly unstable to the formation of a magnetic ground state.

The trend in properties we observe in MBe_{13}, where M=U, Np, and Pu, is consistent with there being a narrow f band at the Fermi energy in UBe_{13} which narrows as Np is added. Perhaps this narrower band, with its necessarily higher electron-electron correlations, is responsible for the suppression of superconductivity well before the onset of magnetism in Np-rich compounds in $U_{1-x}Np_xBe_{13}$. This narrower f band gradually moves lower in energy until it causes a Kondo resonance at $PuBe_{13}$.

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