Anomalous behavior of $PuAl_2$

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We report low-temperature specific-heat measurements on $PuAl_2$. Two anomalies in C are observed, a sharp transition at 3.5 K twice the size of a broader transition at 9.5 K. Specific-heat measurements in an 11 T applied field, coupled with previous resistivity, susceptibility, and NMR results, indicate rather clearly that the lower transition is of magnetic origin, inferred to be due to itinerant antiferromagnetism, while the upper transition is definitely not of magnetic origin, but possibly due to a structural distortion. The rapid change of properties with the 1% change in f atom separation in going from UAl_2 to $NpAl_2$ to $PuAl_2$ is discussed.

I. INTRODUCTION

The low-temperature properties of C-15 structure, MAl_2 compounds, where M contains f electrons, have been of interest for a number of years. In particular, $CeAl_2$ and related pseudobinary compounds have been extensively studied as Kondo systems,[1,2] while UAl_2 (Refs. 3–5) and related pseudobinary compounds [$U_{1-x}Th_xAl_2$,[6] $U_{1-x}La_xAl_2$,[7] $U_{1-x}Y_xAl_2$,[8] $U_{1-x}Pu_xAl_2$ (Refs. 9–11)] have been studied as spin-fluctuation systems. The compound UAl_2 was found[3] in 1975 to have an upturn in the low-temperature specific heat C that followed the predicted[12,13] $T^3 \ln T$ temperature dependence for long-range ferromagnetic spin fluctuations, i.e.,

$$C = \gamma T + \beta T^3 + \delta T^3 \ln(T/T_{SF}) \ , \quad (1)$$

where γT is the normal electronic term; βT^3 is due to the lattice specific heat and T_{SF} is a characteristic spin-fluctuation temperature. This close approach to ferromagnetism is consistent with the observed distance between the U atoms, $d_{U\text{-}U}$, of 3.362 Å, near to the Hill limit[14] of 3.4 Å above which the f electrons in U are expected to become localized. Thus, slight expansions of the lattice by third element substitutions are expected to radically alter not only the magnetic character, but also the electronic density of states at the Fermi energy, proportional to γ in Eq. (1), as the f electrons go towards localization, i.e., the f bandwidth decreases toward zero. The specific heats of both La and Pu substituted UAl_2 have been measured and exhibit sizable increases in γ, 70% in $U_{0.85}La_{0.15}Al_2$ (Ref. 7) and 80% in $U_{0.3}Pu_{0.7}Al_2$ (Ref. 11) versus the $\gamma(=142$ mJ/mole $K^2)$ of pure UAl_2, consistent with La and Pu both being larger than U and causing the lattice to expand. It should be stressed that this progression of γ and also magnetic behavior is an extremely sharp function of the f-atom separation near the Hill limit, e.g., $NpOs_2$, $d_{Np\text{-}Np}=3.258$ Å, is a ferromagnet at 7.5 K while $NpRu_2$, $d_{Np\text{-}Np}=3.230$ Å, does not order down to 1.5 K.[15]

The question of the magnetic order of $PuAl_2$, $d_{Pu\text{-}Pu}=3.3943$ Å, has never been solved. The resistivity of annealed $PuAl_2$, as reported in Ref. 10, rises from 150 $\mu\Omega$ cm at 300 K to a peak value of 220 $\mu\Omega$ cm at 7.5 K, at which point the resistivity falls rapidly to 40 $\mu\Omega$ cm at 1.2 K. No corresponding anomaly is observed in the magnetic susceptibility data[10] down to an unstated temperature around 4 K, with $\chi(T\rightarrow 0)$ for $PuAl_2$ a factor of 3 smaller than that for UAl_2. On radiation damaged $PuAl_2$, the resistivity rises to only about 188 $\mu\Omega$ cm upon cooling from 300 to 50 K, and then remains roughly constant down to lower temperatures.[10] Thus, the mechanism that causes the peak in the resistivity and increased electron scattering (higher resistivity) in annealed $PuAl_2$ is removed by radiation damage. The susceptibility is little changed by damage.[10] The disappearance of the NMR resonance (taken as evidence for magnetism) observed[10] at 6 K in $U_{0.7}Pu_{0.3}Al_2$ and at 4 K in $U_{0.3}Pu_{0.7}Al_2$ was not seen in $PuAl_2$. Instead, increased line broadening of the resonance is observed starting below about 7.5 K and increasing to about 1000 G at 4.2 K. The authors of Ref. 10 found this line broadening, due to an inhomogeneous magnetic interaction, to be anomalous, as such broadening, sometimes found in chemically inhomogeneous systems above a magnetic transition, was not expected in $PuAl_2$ which *higher-temperature* NMR spectra showed to be a well-ordered compound. We will return to this point below. Although antiferromagnetic order was said[10] to be present in one sample of $U_{0.3}Pu_{0.7}Al_2$ at 4 K based on NMR measurements, the specific heat[16] of $U_{0.3}Pu_{0.7}Al_2$ down to 2.4 K showed no anomaly. One would expect, based on results in other systems,[15] that the magnetic behavior in $U_{1-x}Pu_xAl_2$ would follow a monotonic trend with $d_{U\text{-}U}$ *except* for the complication that Pu is also an f-electron atom. Thus, the present work reports on the low-temperature specific heat of $PuAl_2$ between 2.6 and 15 K in 0 and 11 T applied field. These data, in conjunction with the already reported[10] resistivity, magnetic susceptibility, and NMR measurements on $PuAl_2$, demonstrate clearly that the 1% increase in f-atom separation in $PuAl_2$ compared with UAl_2 is accompanied by quite unusual changes in the low-temperature properties.

II. RESULTS

The sample of $PuAl_2$ was prepared by arc melting together the pure constituents, using ^{239}Pu, and remelting three times to ensure homogeneity. The C-15 compound $PuAl_2$ is a congruent melter; that is, the C-15 structure is stable up to the melting point. Debye-Scherrer powder diffractometry exhibited only C-15 structure diffraction lines, with

$a_0 = 7.8387$ Å and $d_{Pu\text{-}Pu} = 3.3943$ Å. In order to avoid any self-damage alteration of properties as discussed in Ref. 10 and summarized above, the specific heat was measured on 4.4 mg of the arc-melted ingot in 0 field and on a 1.7 mg piece to lower temperatures and in 0 and 11 T field starting within one day and finishing within four days of the last melting of the sample. Within this time, no change in the low-temperature specific heat was observed.

The results of the present work for the specific heat of annealed $PuAl_2$ are presented in Fig. 1 along with previous results[11] for UAl_2 and $U_{0.3}Pu_{0.7}Al_2$. Above 12 K, we see reasonable agreement between the data for $PuAl_2$ and $U_{0.3}Pu_{0.7}Al_2$, indicating that the γ, or electronic density of states, of the two compounds is similar. Below 12 K, the specific heat of $PuAl_2$ rises to a peak at 9.5 K. Based on probable slight differences in preparation and time between annealing and measurement, this anomaly at 9.5 K likely corresponds to the resistive anomaly at 7.5 K and the increasing linewidth observed in the NMR data at a similar temperature in Ref. 10.

At yet a lower temperature, the specific-heat data shown in Fig. 1 for $PuAl_2$ go through yet another, much larger and sharper peak at 3.5 K.

What is the nature of these two transitions? First of all, the lower, 3.5 K, transition may correspond to a slight shoulder in the resistivity data,[10] while the susceptibility data[10] show no anomaly below 30 K (although these data may not extend below 4 K). From these remarks, and from the size and sharpness of the specific-heat anomaly shown in Fig. 1, the anomaly is likely some sort of itinerant magnetic transition. We have measured this anomaly in an 11 T magnetic field (see Fig. 2) and find that it shifts downward in temperature by ~ 0.7 K with field. Thus, this lower transition appears to be an itinerant (entropy only $\sim 6\%$ of $R \ln 2$) antiferromagnetic transition. It is interesting to note that C-15 $NpAl_2$, $d_{Np\text{-}Np} = 3.371$ Å, is[15] a local moment ferromagnet at 56 K.

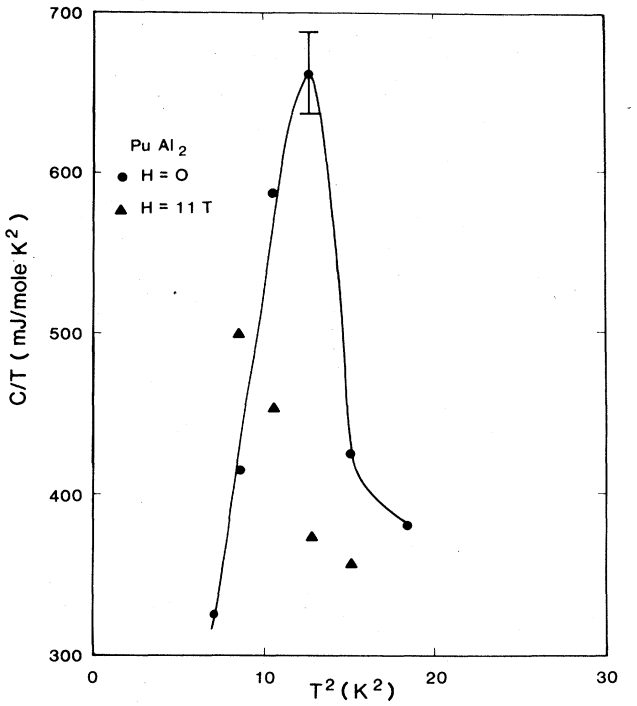

FIG. 2. Expanded view of the low-temperature specific heat of $PuAl_2$ in zero (dots) and 11 T (triangles) applied field. Data in 11 T at the higher, 9.5 K, transition (not shown) indicated no change in field to $\pm 5\%$.

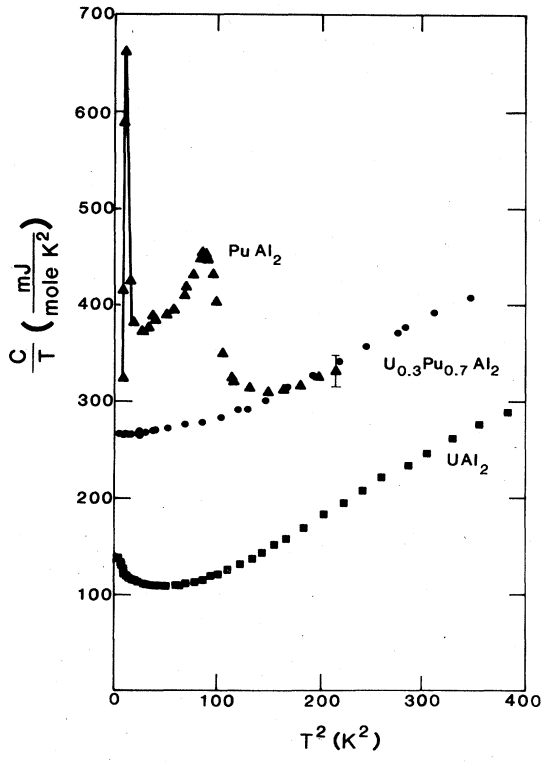

FIG. 1. Low-temperature specific heat of UAl_2 (Ref. 11), $U_{0.3}Pu_{0.7}Al_2$ (Ref. 11), and $PuAl_2$, measured in the present work. The line drawn through the lowest-temperature $PuAl_2$ data is solely a guide to the eye.

The upper transition at 9.5 K, although it corresponds to a large peak in the resistivity, is not seen in the magnetic susceptibility and only broadens, but does not destroy, the NMR resonance. Additionally, we find no field dependence of the specific-heat transition in a 11 T applied magnetic field. Thus, although successive antiferromagnetic transitions have been seen in other materials, e.g., $NdRh_4B_4$,[17] these results argue that the upper peak in C is not of magnetic origin. Although neutron or x-ray diffraction measurements at low temperatures are needed to be certain, we believe our data plus the previously observed[10] inhomogeneous line broadening below 10 K in the NMR data, when the antiferromagnetic transition at 3.5 K was unknown, point to a structural distortion at 9.5 K in $PuAl_2$. This is consistent with the lack of field dependence of the specific-heat data at the transition and the lack of a susceptibility anomaly.

III. CONCLUSIONS

The low-temperature specific heat of $PuAl_2$ has a γ of approximately 260 mJ/mole K^2, similar to that of $U_{0.3}Pu_{0.7}Al_2$. Two anomalies in the specific heat are observed. The ano-

maly at 3.5 K appears to be an itinerant antiferromagnetic transition, as seen also in $NpIr_2$ (Ref. 18) and $NpSn_3$.[19] The anomaly at 9.5 K does not appear to be magnetic in origin. Previous inhomogeneous line broadening NMR results on $PuAl_2$, coupled with the specific-heat data, are consistent with this higher-temperature anomaly being a structural distortion of some kind. A somewhat analogous compound might be CeB_6, where two (significantly larger) anomalies[20] occur in C at 2 and 3 K, with the lower anomaly sharper and larger, and resistivity behavior[21] similar to that in $PuAl_2$ is observed (peak at 3 K, sharp falloff below with a shoulder at the lower transition). The analogy of $PuAl_2$ with CeB_6 is, however, a limited one since the upper anomaly in C in CeB_6 displays significant field dependence, moving upward in temperature by 30% in only a 1.8 T field. Thus, $PuAl_2$ displays unique properties that need to be further investigated.

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