Experimental Electronic Heat Capacities of α- and δ-Plutonium: Heavy-Fermion Physics in an Element

J. C. Lashley,[1,2] J. Singleton,[1] A. Migliori,[1] J. B. Betts,[1] R. A. Fisher,[2] J. L. Smith,[1] and R. J. McQueeney[1]

[1]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*

[2]*Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

(Received 10 June 2003; published 13 November 2003)

We have measured the heat capacities of δ-$Pu_{0.95}Al_{0.05}$ and α-Pu over the temperature range 2–303 K. The availability of data below 10 K plus an estimate of the phonon contribution to the heat capacity based on recent neutron-scattering experiments on the same sample enable us to make a reliable deduction of the electronic contribution to the heat capacity of δ-$Pu_{0.95}Al_{0.05}$; we find $\gamma = 64 \pm 3\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$ as $T \to 0$. This is larger than that of any element and large enough for δ-$Pu_{0.95}Al_{0.05}$ to be classed as a heavy-fermion system. By contrast, $\gamma = 17 \pm 1\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$ in α-Pu. Two distinct anomalies are seen in the electronic contribution to the heat capacity of δ-$Pu_{0.95}Al_{0.05}$, one or both of which may be associated with the formation of the α'-martensitic phase. We suggest that the large γ value of δ-$Pu_{0.95}Al_{0.05}$ may be caused by proximity to a quantum-critical point.

DOI: 10.1103/PhysRevLett.91.205901 PACS numbers: 65.40.Ba, 61.66.Bi, 61.82.Bg, 65.40.Gr

Plutonium represents the boundary between localized (Am) and delocalized (Np) $5f$ electrons in the actinide series [1,2]; the resultant small energy scales, large density of states, and general instability of the $5f$-electron system may be the root cause of many of Pu's extraordinary properties [1–7]. For instance, it is thought that itinerant $5f$ electrons lower their energy by causing Peierls-like distortions, yielding the low-temperature α (monoclinic), β (body-centered monoclinic), and γ (body-centered orthorhombic) phases [6,8]. By contrast, it is believed that some or all of the $5f$ electrons are localized in the δ phase, allowing the Madelung potential of the remaining s, p, and d electrons to produce a higher symmetry face-centered cubic structure [1,2,8]. Very little provocation is required to transform the low-symmetry phases into δ-Pu; the δ phase occurs between 319 and 451 °C in pure Pu and is stabilized to zero temperature by adding a small amount of a trivalent element, such as Al, Ce, or Ga [7].

A reliable estimate of the electronic contribution to the entropy of Pu is a very important key in understanding the difference between the α and δ phases and the dramatic effect of alloying. Unfortunately, attempts to extract relevant information from C_P, the experimental heat capacity [9–16], have been inconclusive because the phonon contribution to C_P was unknown. A traditional way to circumvent this problem is to use low-temperature C_P data; a plot of C_P/T versus T^2, where T is the temperature, is linear at sufficiently low T [17];

$$(C_P/T) = \gamma + \alpha T^2. \quad (1)$$

Here γT and $\alpha T^3 = (12\pi^4 R T^3)/(5\theta_D^3)$ are the electronic and phonon contributions to C_P; θ_D is the Debye temperature [17]. The $T = 0$ intercept γ is a measure of the electronic density of states. Sadly, most measurements of C_P in Pu have been restricted to $T \gtrsim 10$ K, due to problems associated with self-heating caused by radioactive decay [9–16]. In spite of some pioneering work down to $T \approx 7$ K in α-Pu [14] and $T \approx 4$ K in δ-$Pu_{1-x}Al_x$ [15], there is still a considerable spread in the γ values reported in the literature; e.g., in the low-T δ-$Pu_{1-x}Al_x$ measurements [15] the γ values range from 42 to 68 $\mathrm{mJ\,K^{-2}\,mol^{-1}}$.

In this Letter, we report the solution of these problems by (i) measuring C_P for α-Pu and Al-stabilized δ-Pu to significantly lower temperatures than has been previously possible ($T \approx 2$ K), using a sample mount which minimizes the effect of self-heating, and (ii) extracting the electronic component of C_P for δ-$Pu_{0.95}Al_{0.05}$ by subtracting the phonon contribution, deduced using recent neutron-scattering data on the same sample, from the raw data. These procedures show that the electronic contribution to the heat capacity varies linearly with T only when $T \lesssim 10$ K. Moreover, we observe two distinct anomalies in the electronic heat capacity of δ-$Pu_{0.95}Al_{0.05}$, one or both of which may be associated with the α'-martensitic phase observed by optical metallography. By restricting our analysis to suitably low temperatures, we obtain $\gamma = 64 \pm 3\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$ for δ-$Pu_{0.95}Al_{0.05}$ and $\gamma = 17 \pm 1\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$ for pure α-Pu in the limit $T \to 0$. We also observe a large difference in the electronic contribution to the total entropy for α-Pu and δ-$Pu_{0.95}Al_{0.05}$.

The α-Pu sample was prepared by levitation zone refining and distillation as described in Ref. [18]. Starting material was double-electrorefined ^{242}Pu cast into rods. The rods were purified by passing a 10 mm-long molten floating zone (750 °C) 10 times through a cast rod at a travel rate of 1.5 cm/h at 10^{-5} Pa [18]. After this, the impurity level was 174 ± 26 ppm, of which U forms approximately 110 ppm [18]. The δ-Pu specimen was alloyed by arc melting followed by a lengthy anneal at 450 °C. The specimen was formed into a plate by rolling,

 © 2003 The American Physical Society

followed by heat treatments to relieve the cold work. Samples were cut, mechanically polished, chemically polished, and heat treated prior to measurement.

Heat capacity measurements were made using the thermal relaxation method in a Quantum Design PPMS, the performance of which has been subjected to extensive analysis [19]. To counteract the self-heating due to radioactive decay, a modified sample puck with high thermal contact to the heat bath was employed for the low-T data. Measurements comparing the modified puck with a standard one at higher T were identical within experimental error. Measurements made from 10 to 300 K used samples ranging from 20 to 30 mg, while below 10 K, sample masses of 5 to 10 mg were used. Samples were secured to the puck using Apiezon N-grease to ensure good thermal contact. Immediately before each sample was studied, the addenda (puck and grease) were measured over the same T range. All heat capacities shown in the figures are corrected by subtracting the addenda contribution from the raw data; systematic errors (shown as bars) due to inaccuracies in the PPMS [19] and measurement of the sample masses are $\approx \pm 1.5\%$ of C_P.

The heat capacity C_P of δ-$Pu_{0.95}Al_{0.05}$ is plotted versus T in Fig. 1 (solid points). To extract the electronic contribution to C_P, we employ a recent measurement of the phonon density of states $g(E)$ as a function of energy E

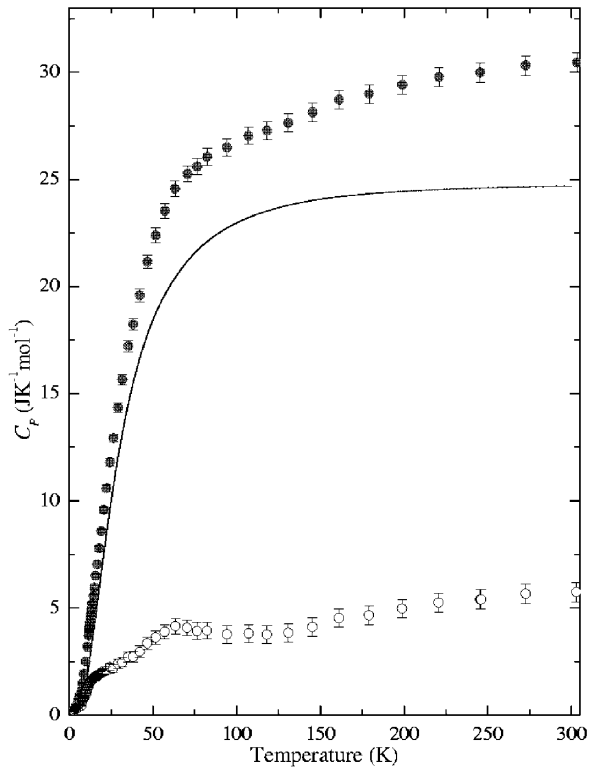

FIG. 1. Experimental heat capacity of δ-$Pu_{0.95}Al_{0.05}$ (filled points: ●) versus temperature. The curve is $C_{P\mathrm{ph}}$, the phonon contribution to the heat capacity. The electronic contribution to the heat capacity ($C_{\mathrm{el}} = C_P - C_{P\mathrm{ph}}$) is plotted as hollow points (○).

carried out on the same sample of δ-$Pu_{0.95}Al_{0.05}$ [20]. Neutron-scattering and sound-velocity data were used to derive $g(E)$ at $T = 27$, 65, 150, and 300 K [20]. The phonon contribution to C_P, $C'_{P\mathrm{ph}}$, was computed using

$$C'_{P\mathrm{ph}} \approx C_{V\mathrm{ph}} = \frac{\partial}{\partial T}\left[\int_0^\infty Eg(E)f(E,T)dE\right]. \qquad (2)$$

Here $C_{V\mathrm{ph}}$ is the phonon heat capacity at constant volume [21], E is the energy, and $f(E,T)$ is the Bose-Einstein distribution function.

Such an approximation neglects anharmonic effects; however, the T dependence of $g(E)$ [20] shows that such effects are small for $T \lesssim 150$ K. More significantly, the computed $C'_{P\mathrm{ph}}$ varied by up to $\pm 1\%$ (i.e., of similar size to the experimental uncertainty in C_P), depending on which $g(E)$ (i.e., that based on the 27, 65, 150, or 300 K data) was used. To minimize the impact of this effect, the phonon contribution to the heat capacity $C_{P\mathrm{ph}}$ plotted in Fig. 1 (curve) is a T-dependent interpolation between the computed $C'_{P\mathrm{ph}}$.

C_{el}, the electronic contribution to C_P of δ-$Pu_{0.95}Al_{0.05}$, was estimated by subtracting $C_{P\mathrm{ph}}$ from the experimental C_P data [21]; C_{el} values are shown as hollow points in Fig. 1 and on an expanded vertical scale in Fig. 2(a). As noted in the discussion of Eq. (1), the expectation for a simple metal is that $C_{\mathrm{el}} = \gamma T$. Even a cursory inspection of Fig. 2(a) shows that the experimental values of C_{el} follow a straight line only through the origin for $T \lesssim 10$ K; between approximately 10 and 40 K, there is a distinct "hump" superimposed on the quasilinear increase, while at $T \approx 65$ K there is a "λ-shaped" maximum, eventually followed by a more gentle increase.

A λ-like feature in the heat capacity is characteristic of a martensitic transition [23]. Support for this attribution comes from the retention of a small fraction of the α' phase, as revealed by the characteristic "tweed" structure shown in a metallographic examination of the sample after thermal cycling (Fig. 3). Neutron-scattering and elastic-moduli data on the same sample before and after cooling [20] and volume-fraction analysis of optical metallography suggest that our δ-$Pu_{0.95}Al_{0.05}$ contains around 5%–7% of the α' phase. Note that a knowledge of the phonon contribution was required to reveal the martensite feature in the heat capacity; until the current work, no clear indication of such a phase has been extracted from the heat capacity of δ-Pu. Moreover, the manifestation of the transition in C_{el} strongly suggests that the transition is electronically driven.

Figure 2(b) shows the effective $\gamma(= C_{\mathrm{el}}/T)$ for δ-$Pu_{0.95}Al_{0.05}$, plotted as a function of T. For $T \lesssim 10$ K, $\gamma \approx 65$ mJ K^{-2} mol^{-1}. Around 10 K, there is a sharp dip, followed immediately by the above-mentioned hump in C_{el}, which appears as a broad peak (maximum at $T \approx 13$ K) in the effective γ. Such a peak suggests a contribution to the electronic entropy associated with a second phase transition at $T \approx 13$ K. This may be linked

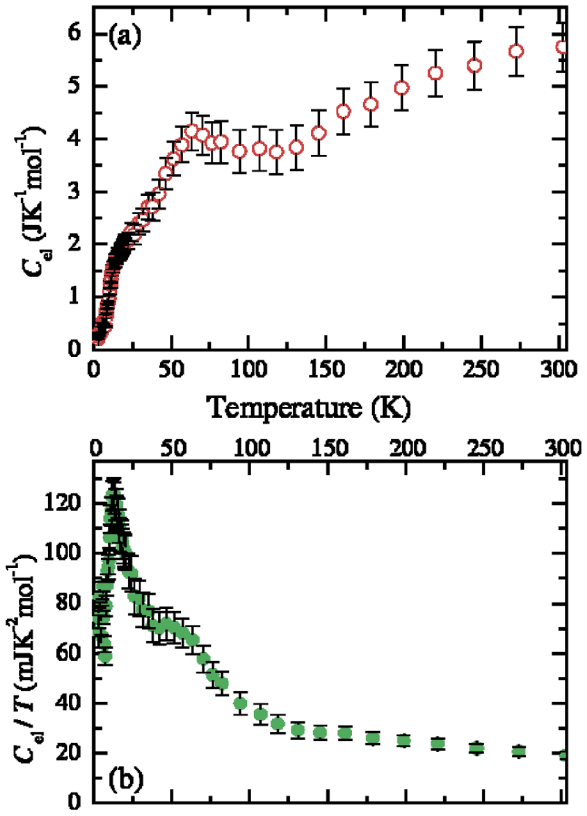

FIG. 2 (color online). (a) Electronic contribution to the heat capacity of δ-$Pu_{0.95}Al_{0.05}$ ($C_{el} = C_P - C_{Pph}$) versus T. (b) The same data plotted as C_{el}/T versus T.

to the λ-like transition seen in C_{el} at $T \approx 65$ K [Fig. 2(a)]; multistage phase transitions have been observed in actinides such as U and predicted in Pu [24].

Above 40 K, C_{el}/T returns briefly to $\gamma \approx 70\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$, before falling gradually to $\gamma \approx 20\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$. This complicated variation illustrates the great importance of low-temperature (i.e., $T \lesssim 10$ K) C_P data. The nonlinear variation of the electronic contribution to the heat capacity with T is the probable reason for the previous, widely varying values of γ and θ_D for δ-Pu quoted in the literature [13,15,16].

Having established that the electronic contribution to the heat capacity of δ-$Pu_{0.95}Al_{0.05}$ is linear in T only below $T \approx 10$ K, we perform a fit of Eq. (1) to the experimental C_P data in this range; this is shown (●) in Fig. 4 which also displays C_P/T for pure α-Pu (○). Similarly, the fit for α-Pu is restricted to $T < 16$ K. The fits of Eq. (1) yield $\gamma = 64 \pm 3\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$ [in good agreement with Fig. 2(b) and lying within the spread of values reported in Ref. [15]] and $\theta_D = 100 \pm 2$ K for δ-$Pu_{0.95}Al_{0.05}$. Likewise, we obtain $\gamma = 17 \pm 1\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$ (i.e., within the range 16–23 $\mathrm{mJ\,K^{-2}\,mol^{-1}}$ reported by Ref. [14]) and $\theta_D = 153 \pm 2$ K for α-Pu.

The value of γ for α-Pu is remarkable enough, being bigger than that of any other element [12,25]; nevertheless, its large size may be understood reasonably conventionally when the $5f$ electrons are taken into account [12].

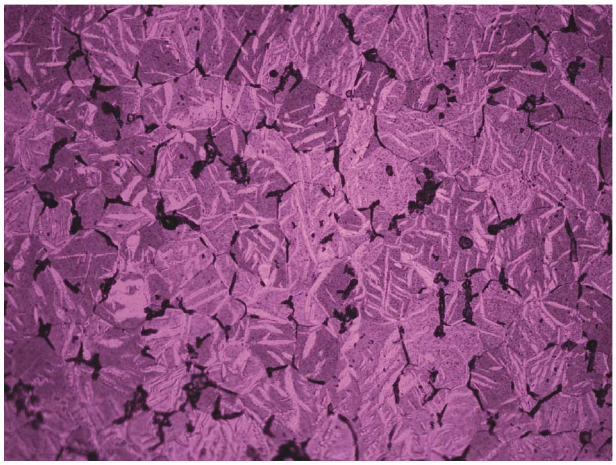

FIG. 3 (color). Optical metallography showing the surface of the δ-$Pu_{0.95}Al_{0.05}$ heat capacity sample after the measurement. The α' martensite phase is identified as the light tweed pattern on the surface. The sample was photographed at 500 ×, and the standard American Society for Testing and Materials method was used to determine a 5%–10 % volume fraction of the martensite (light acicular formations).

However, γ for δ-$Pu_{0.95}Al_{0.05}$ is a factor ~4 bigger, being large enough to class it as a heavy-fermion system [26]. Note that the increase cannot be simply related to the presence of Al, which has a comparatively small value of γ in its pure form [25].

Finally, we compute the specific entropies using

$$S_{el} = \int_0^{300} \frac{C_{el}}{T}\,dT \quad \text{and} \quad S_{total} = \int_0^{300} \frac{C_P}{T}\,dT. \qquad (3)$$

For δ-$Pu_{0.95}Al_{0.05}$, we find that $S_{el} = 11.4\ \mathrm{JK^{-1}\,mol^{-1}}$, of which approximately $2\ \mathrm{JK^{-1}\,mol^{-1}}$ is associated with the peak in C_{el}/T at $T \approx 13$ K; this should be compared with $S_{total} = 68.4\ \mathrm{JK^{-1}\,mol^{-1}}$. By contrast, $S_{total} = 57.1\ \mathrm{JK^{-1}\,mol^{-1}}$ for α-Pu. Although the lack of neutron data means that we do not have a reliable means of extracting C_{el} in α-Pu, an upper bound for S_{el} is given by $300\gamma \approx 5.1\ \mathrm{JK^{-1}\,mol^{-1}}$. Hence, $S_{el}/S_{total} \lesssim 0.09$ for α-Pu, roughly half the value $S_{el}/S_{total} \approx 0.17$ obtained for δ-$Pu_{0.95}Al_{0.05}$. As in the case of γ, the S_{el}/S_{total} values suggest that the role of the electronic system is enhanced on going from the α to the δ phase.

In some respects, the behavior of Pu is similar to models of quantum criticality [27,28], which associate quantum-critical points with rearrangements of the Fermi surface, due either to charge- or spin-density-wavelike reconstruction (analogous to the Peierls-like distortions thought to occur in the α phase [8]) or to the onset of itineracy for previously localized electrons (as may occur in the transition from δ- to γ-Pu [8]). A characteristic feature of a quantum-critical point is the proximity of many excited states to the ground state, consistent with the anomalously large (for an element) value of γ seen in δ-Pu [27]. All of the strange properties of Pu, including the complex phase diagram, may, in fact,

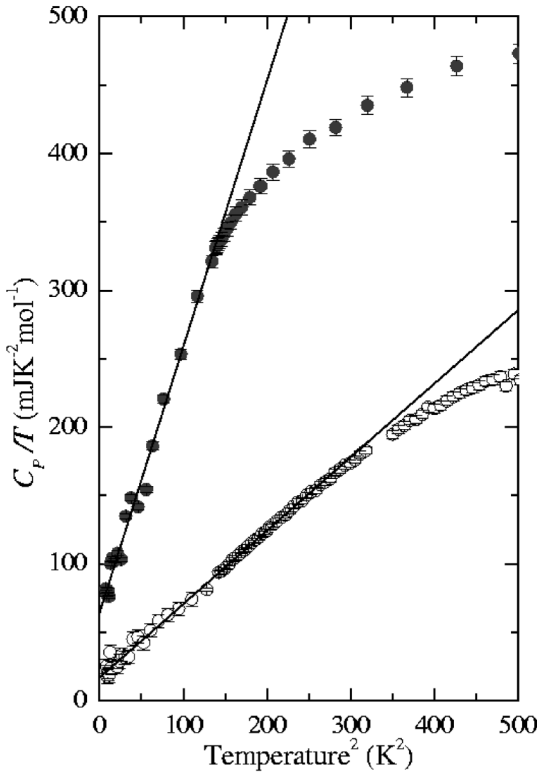

FIG. 4. Low-temperature values of C_P/T for both the pure α-Pu (○) and δ-$Pu_{0.95}Al_{0.05}$ (●) samples plotted as a function of T^2; the low-T portions of the data have been fitted to Eq. (1).

be the result of δ-Pu being close to a quantum-critical point. This could imply that the properties of Pu are "emergent" and not easily derivable from microscopic models.

In summary, we have measured the heat capacities of δ-$Pu_{0.95}Al_{0.05}$ and α-Pu over the temperature range 2–303 K. The availability of data below 10 K plus an estimate of the phonon contribution to the heat capacity based on neutron-scattering data enable us to make a reliable deduction of the low-temperature electronic contribution to the heat capacity of δ-$Pu_{0.95}Al_{0.05}$; we find $\gamma = 64 \pm 3\ \mathrm{JK^{-2}\,mol^{-1}}$. By contrast, $\gamma = 17 \pm 1\ \mathrm{JK^{-2}\,mol^{-1}}$ in α-Pu. We note two anomalies in the electronic contribution to the heat capacity of δ-$Pu_{0.95}Al_{0.05}$, one or both of which may be associated with a martensitic phase transition. The large increase in γ and the electronic contribution to the entropy on going from α- to δ-Pu may be associated with the proximity of δ-Pu to a quantum-critical point.

This work is supported by the U.S. Department of Energy (DOE) under Grant No. LDRD-DR 20030084 "Quasiparticles and Phase Transitions in High Magnetic Fields: Critical Tests of Our Understanding of Plutonium" and by the Primary Physics Program. Part of this work was carried out at the National High Magnetic Field Laboratory, which is supported by the National Science Foundation, the State of Florida, and DOE. We thank Fivos Drymiotis, Mike Ramos, and Ramiro Pereyra for experimental assistance and George Chapline, Neil Harrison, and Chuck Mielke for interesting comments.

[1] S. Y. Savrasov and G. Kotliar, Phys. Rev. Lett. **84**, 3760 (2000).
[2] O. Eriksson *et al.*, J. Alloys Compd. **287**, 1 (1999).
[3] A. J. Arko *et al.*, Phys. Rev. B **62**, 1773 (2000).
[4] J. M. Wills and O. Eriksson, Phys. Rev. B **45**, 13 879 (1992).
[5] S. L. Molodtsov *et al.*, Phys. Rev. Lett. **87**, 017601 (2001).
[6] Per Söderlind *et al.*, Phys. Rev. B **55**, 1997 (1997).
[7] *Plutonium Handbook*, edited by O. J. Wick (American Nuclear Society, La Grange Park, IL, 1980).
[8] A. M. Boring and J. L. Smith, Los Alamos Sci. **26**, 90 (2000).
[9] T. A. Sandenaw, *The Metal Plutonium*, edited by A. S. Coffinberry and W. N. Miner (University of Chicago Press, Chicago, 1961), p. 155.
[10] T. A. Sandenaw, J. Phys. Chem. Solids **23**, 1241 (1962).
[11] J. A. Lee *et al.*, Cryogenics **5**, 227 (1965).
[12] J. A. Lee *et al.*, Proc. R. Soc. London, Ser. A **317**, 303 (1970).
[13] J. C. Taylor *et al.*, *Proceedings of the Conference "Plutonium 1965"* (Chapman and Hall, London, 1967), p. 162.
[14] J. E. Gordon *et al.*, Proc. R. Soc. London, Ser. A **351**, 179 (1976).
[15] G. R. Stewart and R. O. Elliott, *Conference "Actinides-1981" Abstract Booklet* (Lawrence Berkeley Laboratory, Berkeley, CA, 1981), p. 206.
[16] T. A. Sandenaw *et al.*, *Proceedings of the Conference "Plutonium 1960"* (Cleaver-Hume, London, 1961), p. 66.
[17] N.W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Reinhart and Winston, New York, 1976).
[18] J. C. Lashley *et al.*, J. Nucl. Mater. **274**, 315 (1999).
[19] J. C. Lashley *et al.*, Cryogenics **43**, 369 (2003).
[20] R. J. McQueeney *et al.*, report.
[21] In the analysis, we neglect the constant volume to constant pressure correction for the heat capacity, $C_P - C_V = \beta^2 \nu B T$, where β is the volume expansion coefficient, ν is the specific volume, and B is the bulk modulus [22]. Using standard values [7], $\beta^2 \nu B T$ is $\lesssim 0.25\%$ of C_P, at $T = 150$ K, and therefore smaller than typical experimental errors.
[22] A. B. Pippard, *Classical Thermodynamics* (Cambridge University Press, Cambridge, England, 1974), p. 60.
[23] Z. Nishiyama, *Martensitic Transformation* (Academic Press, New York, 1978).
[24] T. Castan *et al.*, Phys. Rev. B **67**, 134113 (2003).
[25] C. Kittel and H. Kroemer, *Thermal Physics* (Freeman and Company, San Francisco, 1980), p. 196.
[26] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, England, 1993).
[27] P. Coleman *et al.*, J. Phys. Condens. Matter **13**, R723 (2001).
[28] M. Oshikawa, Phys. Rev. Lett. **84**, 3370 (2000).