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Specific heats of NpTe and PuTe

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Abstract

The specific heats of single crystals of NpTe and PuTe have been measured in the ranges 1.5–36 K and 5–9.5 K respectively, in a calorimeter designed for small samples. These measurements are the first at sufficiently low temperatures to allow a firm determination of each material's electronic contribution, γT, to its specific heat. Both of these materials were found to be quite metallic in nature, with the γ (in mJ mol^{-1} K^{-2}) for PuTe equal to 30 ± 5 and that for NpTe being 130 ± 10. These data are compared with previous results from other measurements and the implications for understanding the electronic nature of plutonium in PuTe are discussed.

1. Introduction

The electronic ground state and nature of PuTe have been the subjects of considerable discussion, since there does not appear to be a consistent description or explanation for the anomalous physical properties of PuTe. These properties cannot be understood in terms of an integer valence ground state for the plutonium, and a simple intermediate valence state between di- and trivalent plutonium seems to be ruled out by the value of the lattice parameter of PuTe.

The magnetic susceptibility [1, 2] of PuTe (0.26×10^{-3} emu mol^{-1}) is almost temperature independent and much too small for the material to have appreciable f-character at the Fermi energy, E_F. In contrast, both uranium and neptunium pnictides and chalcogenides and the plutonium pnictides in general exhibit magnetic order. Since the small lattice parameter of PuTe (0.619 nm compared with a computed value [3] of 0.672 nm for Pu(II)Te) rules out a divalent, $J = 0$, nonmagnetic ground state for PuTe, it has been proposed [4] that PuTe is a "relativistic semiconductor" with a spin–orbit split-off filled $j = 5/2$ band just below E_F.

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The resistivity of PuTe is almost semiconductor-like in nature. Unfortunately, although the electrical resistivity of PuTe does increase from about 400 $\mu\Omega$ cm at room temperature to about 1200 $\mu\Omega$ cm at 0.65 K, the rise is much too small to be consistent with the calculated [4, 5] semiconducting bandgap of 0.2 eV. Alternatively, neutron measurements have been used to propose [5] that PuTe is a wide-band material that has a low density of states ($N(0)$) at E_F, as found in uranium metal (the orbital component of the magnetic density is also too small for a Pu^{3+} ion). This then would require that its rising, low-temperature resistivity be due to either a large defect contribution, to Kondo-lattice scattering defects, or to both. With regard to NpTe, it has been proposed that it behaves like a heavy fermion system [6] on the basis of its resistivity behavior.

In order to pursue a resolution of these problems and questions, it would be valuable to have data on the specific heat C, for PuTe and NpTe, obtained at sufficiently low temperatures so that $C=\gamma T+\beta T^3$ (*i.e.* that the Debye law for the lattice specific heat is obeyed), and that plots of C/T *vs.* T^2 display a linear relationship where the $T=0$ intercept is γ [α $N(0)$]. Recently the heat capacity of PuTe between 10 and 300 K (some data are shown down to 7.5 K), was reported [7], where the lowest temperature attained was limited by the self-heating accompanying the radioactive decay of 239 Pu. A specific heat coefficient (γ) of 69 mJ mol^{-1} K^{-2} was derived from these data.

However, the above specific heat coefficient was not derived from data at sufficiently low temperatures to be in the Debye limit, as would be desired for accurate extrapolations to zero Kelvin. The present work on PuTe was continued down to 5 K (a factor of a least two lower in T^2) using a small piece (10.2 mg) from a single crystal of PuTe. Similar measurements were also made on 21.6 mg of NpTe. The measurements from both of these materials were obtained using a low-temperature calorimeter designed for small samples, which has been described previously [8].

2. Results and Discussion

The specific heat data for PuTe between 5 and 9.5 K are shown in Fig. 1. The Debye temperatures, proportional to the lattice stiffness, are 200 K if the $T\rightarrow 0$ extrapolation is used, or 175 K derived from the five lowest temperature data points. These data do not agree well with those reported in ref. 7 for the overlapping temperature range; data obtained in the present work at $T\approx 10$ K differ from those in ref. 7 by 15%. Our data are believed accurate to ±5%. The lower temperature data show clearly an additional contribution to the Debye lattice specific heat (*i.e.* C/T *vs.* T^2 is not a straight line). Allowing for the error inherent in these data, as well as the slight amount of curvature in the C/T *vs.* T^2 plot of the data, a value for γ of 30 ± 5 mJ mol^{-1} K^{-2} was derived for PuTe. PuTe is clearly metallic in nature; its specific heat coefficient is similar to that found [9] for α-Pu metal ($\gamma=25$

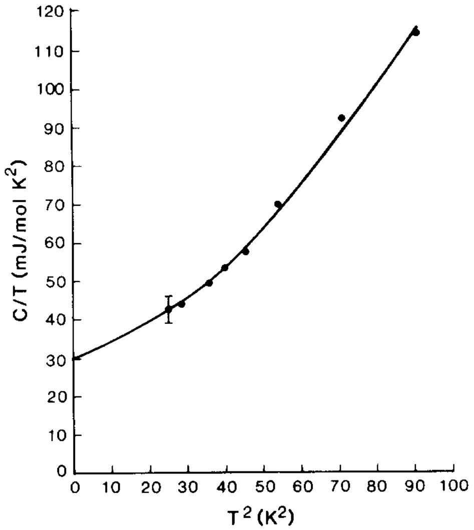

Fig. 1. Plot of specific heat divided by temperature *vs.* temperature squared from single crystals of PuTe.

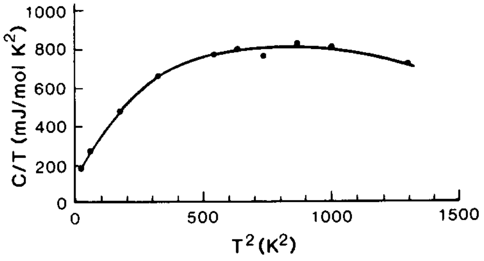

Fig. 2. Plot of the NpTe data (specific heat divided by temperature data *vs.* temperature squared), shown for the range 5–36 K.

mJ mol^{-1} K^{-2}), which has a low-temperature magnetic susceptibility [10] of 0.6×10^{-3} emu mol^{-1}. Thus, the proposal in ref. 5 that PuTe is a broad-band "metal" with a relatively low density of states at E_F is consistent with our present specific heat results. Our data for PuTe have generated a value for the specific heat that is in good agreement with the value of 25 mJ mol^{-1} K^{-2} predicted by Wachter *et al.* [3] for this material. They used a model developed for the samarium chalcogenides that incorporated the concept of an intermediate valence state for the samarium.

In the case of NpTe, susceptibility [11] and resistivity [12] data have been interpreted as indicating antiferromagnetism at 30 K. Our high-temperature specific heat data shown in Fig. 2 do not show a strong ordering peak (*i.e.* there is a limit of less than 0.2 μ_B in any unseen anomaly). The addenda correction to the total measured C is less than 15% at 32 K and decreases as the temperature is lowered. Although the absolute accuracy of

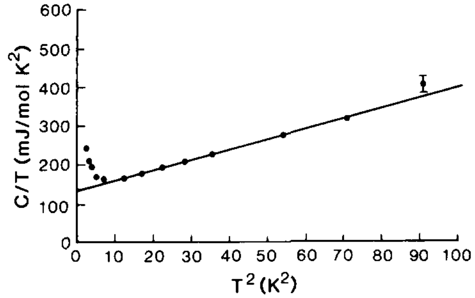

Fig. 3. Plot of NpTe data (specific heat divided by temperature *vs.* temperature squared) for the range 1.5–9.5 K.

these data are believed to be within ±8%, the precision or intercomparability within this set of data is on the order of ±3%, which provides confidence that a significant peak is not present at $T_N = 30$ K. The low-temperature specific heat data shown in Fig. 3 do show a substantial specific heat coefficient of 130 ± 10 mJ mol^{-1} K^{-2}, with an upturn in the C/T data below 3 K that may indicate some low-temperature magnetic transition (the hyperfine field reported [6] for NpTe is not large enough to attribute the low-temperature upswing in C/T for NpTe to a nuclear hyperfine Schottky term). The cause for the upturn in the plot below 3 K is unknown. It would be unusual for a heavy fermion system to begin to display such an upturn in C/T at such low temperatures.

Although a specific heat coefficient of 130 mJ mol^{-1} K^{-2} for NpTe is not of sufficient magnitude to allow it to be classified as a heavy fermion system, it does indicate a substantial narrowing of the f-band in NpTe as compared with the band width inferred for PuTe from its specific heat coefficient of 30 mJ mol^{-1} K^{-2}.

3. Summary

It is believed that these results will help narrow the range of possible explanations for the electronic nature of PuTe. In the complex endeavor of understanding actinide compounds, the usefulness of obtaining specific heat measurements at temperatures as low as can be achieved is once again evident. Further measurements at even lower temperature (*e.g.* specific heat in magnetic fields down to 0.3 K) would be valuable in understanding fully the nature of NpTe. At this time the speculation [6] that NpTe may be a "medium weight" fermion system cannot as yet be ruled out definitively.

Acknowledgments

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References

1 M. Allbutt, R. M. Dell and A. R. Junkison, in *The Chemistry of Extended Defects on Non-Metallic Solids*, North-Holland, Amsterdam, 1970, p. 124.

2 K. Mattenberger, O. Vogt, J. C. Spirlet and J. Rebizant, *J. Less-Common Met.*, *121* (1986) 285.

3 P. Wachter, F. Marabelli and B. Buchler, *Phys. Rev. B*, *43* (1991) 11136.

4 M. S. S. Brooks, *J. Magn. Magn. Mater.*, *63/64*, (1987) 649.

5 G. H. Lander, J. Rebizant, J. C. Spirlet, A. Delapalme, P. J. Brown, O. Vogt and K. Mattenberger, *Physica*, *146B* (1987) 341.

6 J. P. Sanchez, K. Tomala, J. Rebizant, J. C. Spirlet and O. Vogt, *19 èmes Journées des Actinides*, March, 1989.

7 R. O. A. Hall, A. J. Jeffrey, M. J. Mortimer and J. C. Spirlet, *AERE-R-13490*, March, 1990.

8 G. R. Stewart, *Rev. Sci. Instrum.*, *54* (1983) 1.

9 G. R. Stewart and R. O. Elliott, in *Abstracts for Actinides 1981*, LBL Report LBL-12441, (1981) 206.

10 J. J. Katz, G. T. Seaborg and L. R. Morss (eds.), *The Chemistry of the Actinide Elements*, Vol. I, Chapman & Hall, New York, 1986, p. 616.

11 O. Vogt, unpublished data, 1987.

12 E. Pleska, J. M. Fournier, J. Chiapusio, J. Rossat-Midnod, J.-C. Spirlet, J. Rebizant and O. Vogt, *J. Phys.*, *49 C-8* (1988) 493.