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Specific heat measurement on UAl_4

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Abstract

UAl_4 is one of the few binary compounds for which published data on specific heat measurements do not yet exist. We have filled this gap for the temperature range from 1.5 to 12 K. The determined value of the Sommerfeld constant γ is 46 mJ mol^{-1} K^{-2}; the Debye temperature Θ_D is 360 K. The measured sample was prepared in an arc melter, annealed and X-ray tested for phase purity. Measurements of susceptibility and magnetization *vs.* field were also made.

1. Introduction

While reviewing data on binary uranium compounds, we were surprised that we could not find any specific heat data for UAl_4. A search of the literature revealed only the brief verbal report of Leyarovski *et al.* [1] in magnetic flux densities up to 14 T, which were claimed to show evidence of a T^3 ln T term in C below 2.5 K, with no value for γ mentioned. Measurements conducted by Buschow and van Daal [2] on susceptibility and specific resistance show a behaviour which can be described by the model of "localized spin fluctuations" [3].

2. Preparation

According to the phase diagram of Hansen and Anderko [4], UAl_4 is stable below approximately 730 °C and changes into UAl_3 + Al at higher temperatures (see also ref. 5). To keep the structure pure during preparation, a long annealing time is required because of the relative low phase transformation temperature.

We have weighed stoichiometric amounts of uranium with a purity of 99.9% and aluminium of purity 99.999% and melted these together under a purified argon atmosphere in an arc melter four times. The resulting product was wrapped in tantalum foil and sealed into quartz with a 300 Torr argon atmosphere. Afterwards it was annealed at a temperature of 700 °C for 6 weeks.

3. X-ray structure investigation

One part of the sample was finely pulverized and applied on a glass-slide. An X-ray diffraction diagram was then determined using a Siemens D-5000 diffractometer. The sample was measured in reflection.

In indexing the diffracted peaks to the appropriate atomic planes we have followed the investigations of Jesse [6]. Jesse prepared an alloy that consisted of 84% UAl_4 after annealing for 3 weeks (balance, aluminium and UAl_3). He established that it had an orthorhombic structure (space group, *Imma*), with the following lattice constants: $a = 4.397$ Å, $b = 6.251$ Å and $c = 13.714$ Å. Although we prolonged the annealing time to 6 weeks, the amount of extrinsic phases in the present work could not be reduced significantly below the value reported by Jesse.

The lattice constants calculated are, within our error bars, the same as those mentioned by Jesse. The unit cell of UAl_4 consists of 20 atoms. From the structure-

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type table [7] we could learn the atomic position of uranium and aluminium. With this information, we were able to calculate that the shortest U–U distance is 4.37 Å.

4. Specific heat measurements

The specific heat measurement was conducted by a relaxation method (step method) described by Bachmann et al. [8]. A sapphire chip, as a holder for the samples, was connected to a thermal reference block with the thermal conductivity K. The sample was warmed to a level of 1% above the temperature of the thermal reference block. After the heating was switched off, the heat capacity of the system was determined using the relaxation time τ to be $C=K\tau$. After subtraction of other contributions (sapphire, grease etc.), the specific heat of the sample was determined. A plot of the measured data (Fig. 1) shows excellent agreement with

$$\frac{C}{T}=\gamma+\beta T^2$$

The extrapolated value for the electronic contribution to the specific heat is $\gamma=46$ mJ mol^{-1} K^{-2}.

The question that needs to be considered is how important the influence of the external phases is on this value. The Sommerfeld constant of the identified external phase UAl_3 is, according to van Maaren *et al.* [9] $\gamma=41.6$ mJ mol^{-1} K^{-2}. Regarding the influence of the external phase and the accuracy of our measurement on the specific heat (about 3%), one can estimate that $\gamma=46\pm3$ mJ mol^{-1} K^{-2} for UAl_4.

Within our (rather good) precision of measurement, we could not detect any T^3 ln T term in C above 1.5 K (see Fig. 1). Regarding the slope angle, *i.e.* the phonon contribution to the specific heat, one can determine the Debye temperature

$$\Theta_D=\left(\frac{1944\times10^3 n}{\beta}\right)^{1/3}$$

with n the number of atoms per formula unit ($n=5$), β in millijoules per mole per (kelvin)^4 and Θ_D in kelvins. The result is $\Theta_D=360$ K. Regarding the influence of UAl_3 ($\Theta_D=378$ K, according to van Maaren *et al.* [9]), one can calculate a Debye temperature Θ_D of 360 ± 10 K for UAl_4.

5. Magnetic measurements

A molar susceptibility of about 1.45 memu mol^{-1} at 2 K is measured. The magnetic moment depending on the field shows no saturation up to 55 kG. In comparing our measurement with the χ *vs.* γ plot for superconductors suggested by Fisk *et al.* [10], one can see that UAl_4 lies near the line for the free-electron Sommerfeld relation (Fig. 2).

6. Summary

Through measurements on its specific heat we have found for UAl_4 a Sommerfeld constant γ of 46 ± 3 mJ mol^{-2} K^{-2} and a Debye temperature Θ_D of 360 ± 10 K. The comparative large U–U distance of 4.37 Å (Hill limit, 3.4 Å) the relative small value of $\chi(1.8\text{ K})=1.45$ memu mol^{-1}, as well as the value of the electronic part of the specific heat are evidence for the presence of hybridization between the 5f electrons and the Al s–p electrons. Measurements of the magnetic susceptibility show no sign of any magnetic ordering down

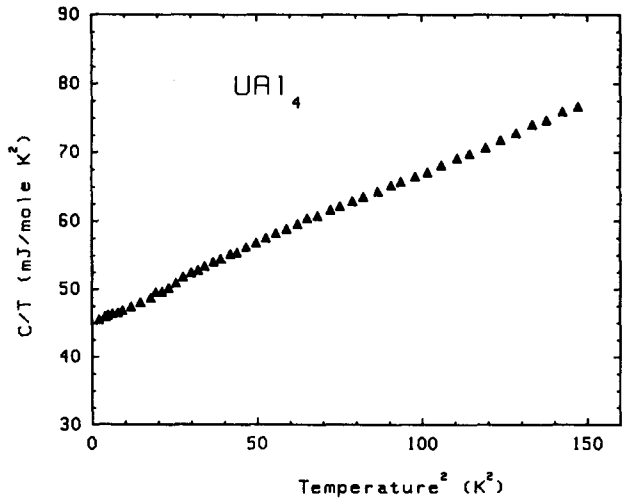

Fig. 1. Specific heat measurement of UAl_4 in the diagram C/T *vs.* T^2.

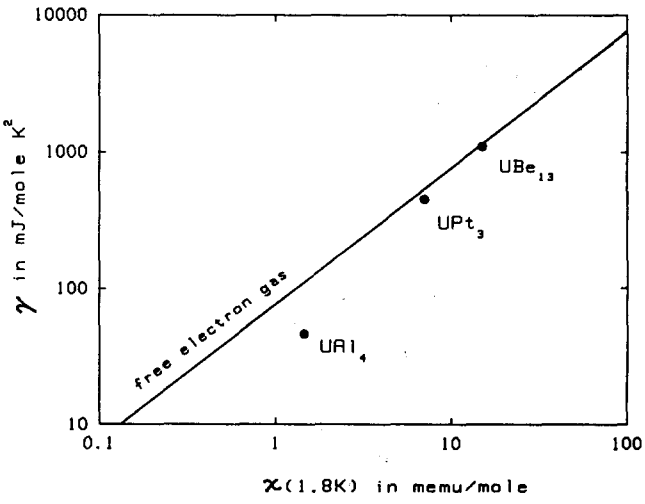

Fig. 2. Position of UAl_4 in the χ *vs.* γ plot. (Data for UPt_3 and UBe_{13} from the work by Stewart [11]).

to 1.8 K. As shown in Fig. 2, data for UAl_4 lie near the Sommerfeld line. Hence this compound, in analogy with U_2PtC_2, may show a tendency to heavy-fermion behaviour. Doping experiments, with aluminium being substituted, as well as specific heat measurements below 1.5 K, could give further information on the nature of 5f electrons in this structure.

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