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LOW TEMPERATURE SPECIFIC HEAT AND ELECTRICAL RESISTIVITY OF $UCu_{4.5}Al_{7.5}$ *

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ABSTRACT

The specific heat and electrical resistivity results are presented for $UCu_{4.5}Al_{7.5}$, a magnetically ordered nearly heavy fermion compound. The specific heat data do not indicate the expected anomaly characteristic for the magnetic order transition; only a very weak one was detected, which has been separated using a simple theoretical procedure. The electronic specific heat coefficient has been estimated to be 118 mJ mol^{-1} K^{-2}. The other heavy fermion coefficients have also been calculated. The electrical resistivity data for $UCu_{4.5}Al_{7.5}$ include indications of strong crystal field effects.

INTRODUCTION

During the investigation of $(U,Th)T_xAl_{12-x}$ compounds, which crystallize with tetragonal crystal structure of $ThMn_{12}$-type and space group $I4/mmm$, we have obtained $UCu_{4.5}Al_{7.5}$. We began this research to elucidate the uranium contribution to the exchange interactions in these compounds, in which the uranium–uranium separation ($\sim$ 0.5 nm) is much larger then the Hill limit [1], and the uranium atoms are diluted in a metallic matrix. Preliminary structural [2] and magnetic investigations [3] of this compound failed to reveal any anomaly in magnetic susceptibility, whereas our subsequent studies [4] showed a maximum in magnetic susceptibility at 30 K,

* Dedicated to Professor Edgar F. Westrum, Jr., in honour of his contribution to calorimetry and thermal analysis and on the occasion of his 70th birthday.

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which was interpreted as the Néel temperature. Moreover, a lack of a resonance on ^{63}Cu in the NMR spectrum [4] could suggest a magnetic ordering, although its origin was not clear (U or Cu moments). It must be pointed out that we were unable to obtain the stoichiometric phase UCu_4Al_8; there were always two phases present, UCu_4Al_8, the major phase, and UAl_3, the minor phase. We did not observe any difference between the magnetic properties of the non-stoichiometric and the stoichiometric phases, because UAl_3 is paramagnetic with almost temperature-independent paramagnetism [5]. In order to extend our knowledge about $UCu_{4.5}Al_{7.5}$, we began our series of measurements of low temperature specific heat and electrical resistivity.

EXPERIMENTAL

$UCu_{4.5}Al_{7.5}$ was obtained by arc-melting as has been previously described [4]. The lattice constants determined from the powder X-ray patterns on a standard diffractometer are $a = 0.8792$ and $c = 0.5122$ nm. Both the specific heat and electrical resistivity measurements were performed independently in the Technische Hochschule in Darmstadt and in the Institute of Low Temperature in Wrocław. The specific heat data on the polycrystalline samples were collected in the temperature ranges of 20–45 K (Darmstadt) and of 4.2–80 K, with no data between 40 and 45 K (Wrocław), representing the dead temperature region between germanium and platinum thermometers. In both laboratories, the standard set-up with the adiabatic calorimeter was used and in both cases, the data were collected using a step-wise method. The results are in good agreement for both experiments in the appropriate temperature region. The electrical resistivity studies were performed using a standard d.c. four-probe method in the temperature range 4.2–300 K, in both cases; these results were also consistent.

RESULTS AND DISCUSSION

The experimental specific heat data denoted C_p^{exp}, are presented in Fig. 1(a). Unexpectedly, we did not detect an anomaly near 30 K characteristic for the phase transition to a magnetically ordered state. Instead, a hardly visible anomaly occurred in the region between 20 and 30 K.

In order to separate this weak anomaly, the theoretical lattice and electronic specific heat contributions were calculated, which are marked in Fig. 1a as C_v^{lat} and C_p^{el}, respectively. The anomaly, separated by subtraction of both the above contributions from the experimental specific heat data, is shown in Fig. 1(b).

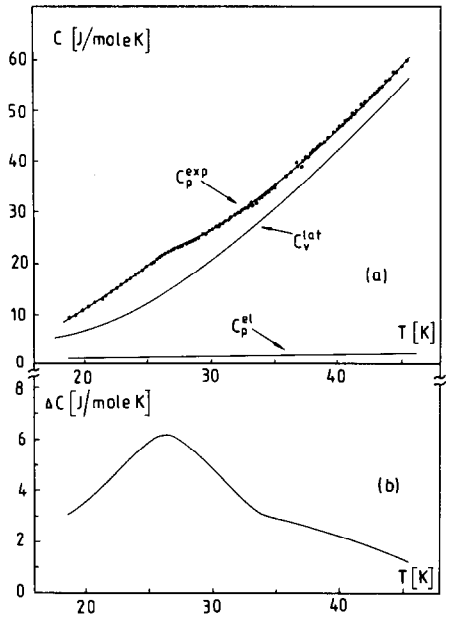

Fig. 1. Temperature dependence of (a) experimental specific heat C_p^{exp} and calculated lattice C_v^{lat} and electronic C_p^{el} specific heat contributions and (b) the anomaly separated by subtraction $\Delta C = C_p^{exp} - C_v^{lat} - C_p^{el}$ for $UCu_{4.5}Al_{7.5}$.

The theoretical lattice contribution to the total specific heat was calculated on the basis of the Neumann and Kopp empirical rule [6] which says that the specific heat is, in some cases, a simple sum of the atomic specific heats of the component elements. This rule is often valid for intermetallic compounds. The Debye model was used for the atomic lattice specific heat contributions and the final formula took the form

$$C_v^{lat} = \left[f_D\left(\frac{\theta_D^U}{T}\right) + 4.5 f_D\left(\frac{\theta_D^{Cu}}{T}\right) + 7.5 f_D\left(\frac{\theta_D^{Al}}{T}\right)\right] 3R$$

Where $f_D(\theta_D/T)$ is the Debye function defined as

$$f_D\left(\frac{\theta_D}{T}\right) \equiv \frac{3}{x^3}\int_0^x \frac{x^4 e^x \, dx}{(e^x - 1)^2} \quad \text{and} \quad x \equiv \frac{\theta_D}{T}$$

θ_D is the Debye temperature and R the gas constant. We took the following values for the Debye temperatures of the component elements [6]: $\theta_D^U = 200$ K; $\theta_D^{Cu} = 310$ K; and $\theta_D^{Al} = 385$ K. In the subtraction procedure, the discrepancy between the lattice specific heat values calculated at constant volume C_v^{lat} and at constant pressure C_p^{lat}, can be neglected within this rough approximation.

In order to estimate the electronic contribution to the total specific heat, C_p^{exp}/T was plotted against T^2 in the temperature range 4.2–16 K (see

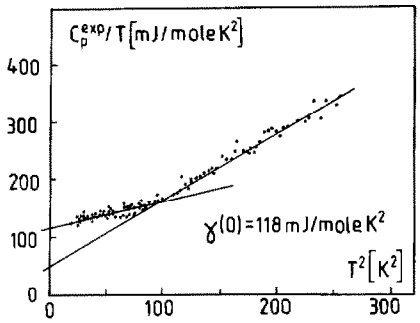

Fig. 2. The C_p^{exp}/T vs. T^2 function for $UCu_{4.5}Al_{7.5}$ plotted in the 4.2–16 K temperature range.

Fig. 2). Extrapolating to zero K, the electronic specific heat coefficient $\gamma(0)$ is equal to 118 mJ mol^{-1} K^{-2}, which represents a much enhanced value. The C_p^{exp}/T against T^2 plot changes its slope near 10 K and the $\gamma'(0)$ obtained by extrapolation to zero K from above 10 K is smaller, being 50 mJ mol^{-1} K^{-2}. This latter value was used to estimate the C_p^{el} contribution shown in Fig. 1(a).

It should be emphasized that the procedure described above has only qualitative value and cannot be applied to the magnetic entropy calculations. Such calculations will be possible when the specific heat measurements now in progress on the $ThCu_{4.5}Al_{7.5}$ reference compound are completed.

The lack of a specific heat anomaly in the region of the magnetic transition, as we found for $UCu_{4.5}Al_{7.5}$, is not an isolated case among antiferromagnetically ordered uranium compounds. Similar behaviour was discovered in the series UN, $UN_{1.59}$ and $UN_{1.73}$ [7] as well as in UNiAl [8] and USe_2 [9]. It is mostly explained in the literature as being caused by crystal field effects or the itinerant nature of magnetic ordering. However, in our case the itinerant character of magnetic ordering can be excluded because of the results of neutron diffraction experiments, in which the value of the uranium ordered magnetic moment was determined to be 1.3(5) μ_B below the T_N of 37(2) K [10].

As mentioned above, the electronic specific heat coefficient $\gamma(0)$ has an enhanced value, which may indicate a heavy fermion-like behaviour at low temperatures. This hypothesis is supported by the high magnetic susceptibility, of the order of 5×10^{-3} emu mol^{-1}, at zero K temperature. The large U–U distance is also a common feature of heavy fermion compounds.

The theoretical coefficients, usually reported for heavy fermions, were also calculated for $UCu_{4.5}Al_{7.5}$. Firstly, the R coefficient, involving the zero K magnetic susceptibility and $\gamma(0)$ values, was estimated to be approximately 3, which is consistent with the DeLong criterion [11]. Next, the R_w coefficient, known as the Wilson ratio, was found to be around 1, which is in

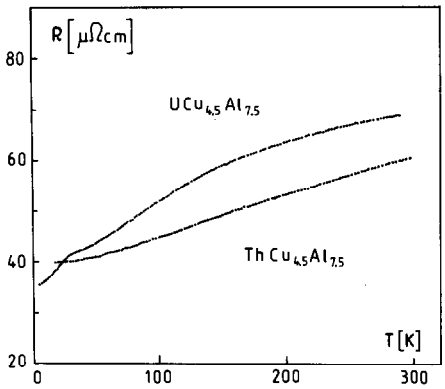

Fig. 3. Temperature dependence of the electrical resistivity data for both (U,Th)$Cu_{4.5}Al_{7.5}$ compounds.

agreement with the Stewart criterion [12], placing $UCu_{4.5}Al_{7.5}$ in the region of magnetically ordered heavy fermion compounds. The heavy electron mass, theoretically estimated under the rough assumption of a spherically symmetric Fermi surface and the +4 valence of uranium ions, is equal to 29 times the free electron mass.

Also, in the case of the UNiAl compound mentioned above, the enhanced value of $\gamma(0)$ was reported to be 167 mJ mol^{-1} K^{-2}.

The temperature dependence of the electrical resistivity for both $UCu_{4.5}Al_{7.5}$ and $ThCu_{4.5}Al_{7.5}$ are presented in Fig. 3.

The resistivity data for the $ThCu_{4.5}Al_{7.5}$ reference compound do not exhibit any anomaly and are typical for non-magnetic transition metals. In contrast, the electrical resistivity curve for $UCu_{4.5}Al_{7.5}$ shows a small anomaly in the range of the magnetic order transition and in two other characteristic regions. In the first one, below 10 K, the resistivity data change in proportion to the T^2 term, which may arise from the heavy fermion behaviour remarked upon earlier. In the second, extending from 70 to 300 K, a negative logarithmic curvature is observed. Such behaviour may indicate a strong electron scattering mechanism at higher crystal field levels [13], in our case of uranium ions. The strong crystal field effects can be responsible for the small entropy of magnetic transition observed in $UCu_{4.5}Al_{7.5}$. The analysis of the temperature dependence of the magnetic susceptibility for $UCu_{4.5}Al_{7.5}$, based on the crystal field level diagram, will be published elsewhere [14].

The R/R_0 resistivity ratio is rather small for $UCu_{4.5}Al_{7.5}$ and does not exceed 2 in the 4.2–300 K temperature range. The residual resistivity value R_0 is relatively high, as is commonly observed for heavy fermion systems. However, we have to point out that this high R_0 value may also arise from the many crystal structure defects, which may occur in polycrystalline samples of ternary intermetallics. Our attempts to improve the quality of the

sample were unsuccessful, because after any annealing process we observed an increase in the UAl_3 minor phase. Therefore, we can conclude that $UCu_{4.5}Al_{7.5}$ may be a metastable compound.

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