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# Low-temperature specific heat for off- and near-stoichiometric UAsSe

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## Abstract

Two UAsSe single crystals with slight variations of the As/Se content ratio have been investigated. The development of the low- $T$  upturn in the resistivity is accompanied by smooth decrease of the Curie temperature. The sample with  $T_C = 116.9$  K and almost invisible upturn could be regarded as a near-stoichiometric, slightly disordered one, whereas the specimen with  $T_C = 101.5$  K appears to be an off-stoichiometric, more strongly disordered one. Clear differences between both electronic and lattice contributions to the specific heat for off- and near-stoichiometric UAsSe crystals have also been found. We ascribe the smaller low- $T$  specific heat for the off-stoichiometric sample in comparison to the near-stoichiometric one to a weaker hybridization between 5f and conduction-electron states accompanied by the relative shift of 5f band with regard to  $E_F$ .

## 1. Introduction

Uranium pnictochalcogenides UXY, where X = P, As, Sb and Y = S, Se, Te, order ferromagnetically along the  $c$  axis. All UXY are recognized as metallic tetragonal compounds whose 5f electrons, according to early magnetic and photo-emission data, are believed to be quite well localized [1,2]. Polarized neutron diffraction measurements for UAsSe also indicate a picture of localized 5f electrons [3]. Unexpectedly, the results of optical and magneto-optical Kerr spectra measurements suggest a narrow 5f band at the Fermi energy,  $E_F$ , rather than a localized 5f state in UAsSe [4,5]. Oppeneer et al. [6] have investigated the magneto-optical Kerr spectra of UAsSe using first-principles energy-band calculations. They have obtained, within a band-like description of the 5f elec-

trons, good agreement with the measured optical spectra and find that the uranium 5f states in UAsSe exhibit at least partially itinerant 5f-electron behavior. They conclude that the 5f electrons are delocalized in the  $ab$ -plane, but localized along the  $c$ -axis. Recent measurements of the angle-resolved photoelectron spectroscopy (ARPES) strongly hint at itinerancy of 5f electrons even in the ferromagnetically ordered state [7,8]. Further on, the latter experiment shows that the f and d bands are more strongly renormalized than the p bands.

UAsSe crystallizes in the tetragonal PbFCl crystal structure [9] (one crystallographic position of uranium ions) and undergoes a ferromagnetic phase transition around 110 K. UAsSe, which belongs to so-called hard ferromagnets with coercive force close 0.8 T for  $H \parallel c$ , is the most frequently investigated system among all uranium pnictochalcogenides. This is because of its unusual low- $T$  transport properties, especially the upturn in the resistivity far below the ferromagnetic transition. The origin of this upturn is very intriguing but not yet clarified.

The electrical resistivity,  $\rho(T)$ , of UAsSe is strongly

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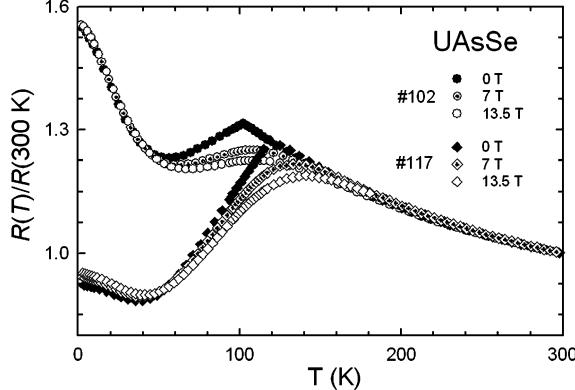


Fig. 1. Temperature dependence of the *ab*-plane resistivity normalized to its room-temperature value in different magnetic fields ( $H \parallel c$ ) for two single crystals of UAsSe with various  $T_C$ .

sample dependent. The measurements showed that the Curie temperature,  $T_C$ , as well as the low- $T$  upturn in  $\rho(T)$  are very sensitive to small variations of the As/Se content ratio [10]. The latter quantity seems to be responsible for the possible disorder in the anionic sublattice. Although there is not yet unquestionable evidence for it, the X-ray as well as the neutron-diffraction experiments, clearly hint at such a possibility [11].

In spite of many papers concerning transport properties of UAsSe [10,12,13], there is only one that deals with its specific heat,  $C(T)$ , [14]. This 20-year-old result was obtained on a powder sample pressed into a pellet together with a silver powder. An enhanced Sommerfeld coefficient,  $\gamma = 41 \text{ mJ/K}^2 \text{ mol}$ , was found and since then is often considered as an indication of the tendency towards itinerancy of the 5f electrons in UAsSe.

Very recently we have briefly reported on the sample dependent low- $T$  specific heat of UAsSe [15]. These systematic measurements have been done using high-quality single crystals. The  $\gamma(T_C)$  dependence showed a minimum close to  $T_C = 111 \text{ K}$ . The observed decrease of  $\gamma$  upon increasing  $T_C$  up to 111 K was attributed to a reduction of the concentration of dynamical scattering centers. The subsequent rise of  $\gamma(T_C)$  for  $T_C > 111 \text{ K}$  signals an additional contribution. Its origin will be discussed in this paper.

## 2. Experimental

The uranium arsenoselenide single crystals were grown by the chemical vapor transport method. Metallic U as well as As and Se in the desired molar ratio was sealed in an evacuated silica tube together with bromine as transport agent. About 3–5 mg of  $\text{Br}_2$  per cubic centimeter of the ampoule volume was used. At the first step, with a gradual increase of temperature from 400 to 950 °C, the elements reacted giving a powder product. Next, the UAsSe substrate

was homogenized for a few days. Finally, the ampoule was placed in a temperature gradient for a few weeks. The transport occurred from the hotter (950 °C) to the cooler (900 °C) part of the tube.

In order to obtain specimens with various  $T_C$  values, different starting conditions, mainly concerning various As/Se substrate ratio, were applied. The above conditions resulted in a few series of plate-like UAsSe single crystals, from which the specimens with extreme  $T_C$  equal to 101.5 and 116.9 K were chosen for further investigations. To simplify the following discussion, we will denote these crystals by #102 and #117, respectively.

For the specific-heat experiments commercial ‘microcalorimeters’ were utilized (Quantum Design and Oxford Instruments in the temperature range 0.4–7 and 1.7–150 K, respectively). The mass of the investigated single crystals was about 15 mg. The electrical resistivity was measured by the standard four-point ac method in the temperature range 1.5–300 K. Low-resistance electrical contacts were made by the touch-welding technique ( $\phi 25 \mu\text{m}$  gold wires).

## 3. Results and discussion

The origin of the upturn in the resistivity of UAsSe upon cooling far below the ferromagnetic transition is still unclear. The size of the low- $T$  upturn can be quantified, e.g. by the  $\text{RR} = R(4.2 \text{ K})/R_{\min}$  ratio, where  $R_{\min}$  is the minimum resistance in the ferromagnetic state.

Fig. 1 displays the *ab*-plane  $R(T)/R(300 \text{ K})$  dependencies for the single crystals #102 and #117 in different magnetic fields. The very small magnetoresistivity, far below the ferromagnetic transition in fields up to 13.5 T, points at a non-magnetic mechanism responsible for its unusual low- $T$  transport properties. It is very likely that the expected disorder in the anionic sublattice determines the low- $T$   $\rho(T)$  dependence of UAsSe [10,15]. The behavior of the sample #102 is very similar to the specimen  $n = 1$  from Ref. [10], as far as  $T_C (= 101.5 \text{ K})$  and the size of the low- $T$  upturn ( $\text{RR} = 1.27$ ) are concerned. For crystals with  $T_C \approx 102 \text{ K}$ , an  $\text{As}/\text{Se} \approx 0.9$  ratio, i.e. chemical composition  $\text{UAs}_{0.94}\text{Se}_{1.06}$ , has been estimated [10]. A qualitatively different behavior is found for sample #117. The weak upturn ( $\text{RR} = 1.03$ ) is accompanied by the highest  $T_C (= 116.9 \text{ K})$  among all literature data concerning UAsSe. We emphasize that for the  $R(T)/R(300 \text{ K})$  dependencies presented in Fig. 1 there have been found extreme values of RR accompanied by the extreme  $T_C$ .

Unfortunately, due to irregular shapes of the samples, we could not precisely determine the resistivity. On the other hand, the  $\rho(T)$  dependence for the sample #102 is very similar to that reported in Ref. [10]. Therefore, we assume the same value of  $\rho(300 \text{ K}) = 275 \mu\Omega \text{ cm}$  for all the UAsSe single crystals with the lowest  $T_C$  (i.e.  $\text{As}/\text{Se} \approx 0.9$ ). It is interesting that our rough estimation of  $\rho(300 \text{ K})$  for the

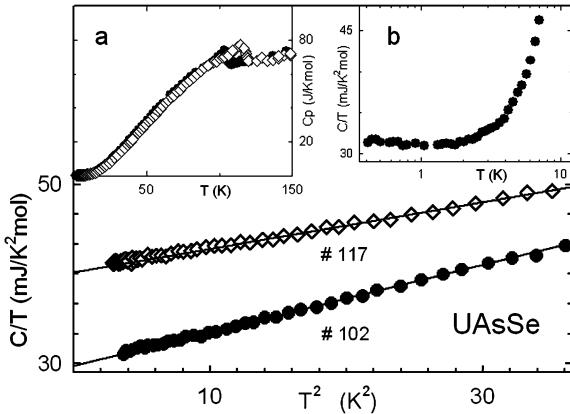


Fig. 2. The low-\$T\$ specific heat, as \$C/T\$ vs \$T\$, of two UAsSe single crystals between 1.7 and 6 K. The measurements have been done on the same crystals as in Fig. 1. The solid lines show the \$\gamma T + \beta T^3\$ dependence, where the fitting \$\gamma\$ and \$\beta\$ parameters were determined from the temperature range 1.7–4.2 K. The different slopes of the solid lines indicate different \$\Theta\_D\$ for both samples. Inset (a): \$C\_p\$ vs \$T\$ for both crystals up to 150 K. Inset (b): \$C(T)/T\$ of the sample #102 down to 0.4 K.

specimen #117 yields also \$240 \pm 50 \mu\Omega\$ cm. A room-temperature resistivity close to \$250 \mu\Omega\$ cm was independently observed by Schoenes et al. [12] for a sample with \$T\_C \approx 108\$ K showing the low-\$T\$ upturn in between those presented in Fig. 1. From this, we conclude that \$\rho(300\$ K) of UAsSe does not change very much with \$T\_C\$ and is close to \$250 \mu\Omega\$ cm. The observed differences are still within margins of error. The second important feature of the electrical resistivity of UAsSe is the universal \$R(T\_C)/R(300\$ K) \$\approx 1.3\$ ratio for all samples measured by us. Such a value has been confirmed in other studies [12]. Both features give a clear hint concerning the \$\rho(T)\$ dependence of UAsSe in its para- and ferromagnetic state. Above \$T\_C\$, its \$\rho(T)\$ behavior seems to be almost sample independent. The situation is quite different below \$T\_C\$. Here, strong sample dependence has been found. The low-\$T\$ upturn in the ferromagnetic state rapidly increases with the smooth decrease of \$T\_C\$.

In our opinion, the very small low-\$T\$ upturn, as well as the highest \$T\_C\$ of the sample #117, points to its small disorder as well as a stoichiometry in the anionic sublattice close to 1:1. Vice versa, crystal #102 could be considered as an off-stoichiometry sample (As/Se \$\approx 0.9\$) with stronger disorder.

In Fig. 2, we show specific-heat data, as \$C/T\$ vs \$T^2\$, obtained between 1.5 and 6 K for the single crystals #102 and #117. The differences between off- and near-stoichiometric specimens are clearly seen both in the size of the \$C(T)/T\$ values and in the slopes of the \$C(T)/T\$ vs \$T^2\$ data. These correspond to the differences in the Sommerfeld coefficient, \$\gamma\$, and the Debye temperature, \$\Theta\_D\$, respectively. \$\gamma\$ values equal to 29.7 and 40.6 mJ/K\$^2\$ mol as well as \$\Theta\_D\$ values equal to 252 and 307 K were found for single crystals

#102 and #117, respectively. We wish to point out that \$\gamma\$ for crystal #117 is in very good agreement with the 20-year-old data published by Blaise et al. [14] (\$\gamma = 41\$ mJ/K\$^2\$ mol and \$\Theta\_D = 233\$ K).

Besides the ferromagnetic transition, there is no additional high-temperature anomaly which could influence the low-\$T\$ specific heat of UAsSe (see inset (a) of Fig. 2). The measurement of the sample #102 down to 0.4 K also does not show any additional phase transition (see inset (b) of Fig. 2). The small \$C(T)/T\$ increase upon cooling below 1 K probably results from the nuclear hyperfine field of the arsenic nuclei.

Taking the validity of the Debye model at low temperatures, \$T < \Theta\_D/50\$ [16] for granted, our analysis of the \$C(T)\$ data was done in the 1.7–4.2 K temperature range. A distinct difference in \$\Theta\_D\$ (>20%) between the single crystals #102 and #117 cannot be simply explained by differences in the stoichiometry. In fact, even a complete substitution of Se for As leads to very small change of the molecular weight (around 1%).

In metals, the conduction electrons give a specific heat proportional to \$T\$ and the phonons give a \$T^3\$-term at low temperatures. In the ferromagnetic state, the magnon contribution to the specific heat, \$C\_{\text{ferro}}\$, is proportional to \$T^{3/2}\$. A distinction of the magnetic \$T^{3/2}\$-term from the electronic one could be easily made only for the systems with sufficiently high \$T\_C\$ because, at temperatures lower than \$T\_C/5\$, the magnetic contribution is usually treated as being negligible [16]. In the UAsSe case, the \$T\_C/5\$ value corresponds to 20 K, which is almost five times higher than the upper temperature limit of our analysis (i.e. 4.2 K). Therefore, we have neglected \$C\_{\text{ferro}}\$ at low temperatures for UAsSe.

Our preliminary specific-heat experiments in the magnetic field (\$H \parallel c\$) do not show a significant difference between the zero-field and the 14 T data for sample #117. This means another contribution of magnetic origin to \$C(T)\$ (e.g. being a result of a polydomain structure) should be ruled out.

As already mentioned, the low-\$T\$ transport properties of UAsSe seem to be influenced by the disorder in the anionic sublattice. In the disordered structure an additional contribution to the specific heat due to a small structural rearrangement caused by the tunneling processes could be observed at low temperatures. These tunneling processes contribute like \$T^n\$, where the exponent \$n\$ is close to 1 [17]. Such a \$T^n\$-term in \$C(T)\$ is usually of the order of a one-tenth of a mJ/K mol at 1 K [17]. The discussed difference in \$\gamma\$ between the crystals #102 and #117 is two orders of magnitude larger and, therefore, cannot be explained by the types of tunneling processes discussed before.

Recently, we have briefly pointed to the possibility of other tunneling processes in UAsSe, i.e. electron-assisted ones, in which the scattering of a conduction electron off the tunneling atom induces the transition [15]. The monotonic decrease of RR with smooth increase of \$T\_C\$ was related to a progressive reduction of the scattering-center

Table 1  
Characterization of the single crystals used for the examination

Single crystal	As/Se <sup>a</sup>	$T_C$ <sup>b</sup> (K)	$\gamma$ (mJ/K <sup>2</sup> mol)	$\Theta_D$ (K)	$V$ (Å <sup>3</sup> )	$R(4.2\text{ K})/R_{\min}$	$\rho(300\text{ K})$ (μΩ cm)	$R(T_C)/R_{300\text{ K}}$
#102	0.75	101.5	29.7	252	134.37	1.27	275	1.31
#117	1.00	116.9	40.6	307	132.44	1.03	$240 \pm 50$	1.27

<sup>a</sup> Ratio of the substrates.

<sup>b</sup> Estimated from the temperature derivative of the resistivity.

concentration [18]. It is predicted that the electron-assisted tunneling processes affect the thermodynamic properties and could lead to large values of specific heat [19]. It follows that the smallest low- $T$  specific heat should be observed for the less strongly disordered specimens. Unexpectedly, a systematic study showed a minimum of  $\gamma(T_C)$  close to  $T_C \approx 111\text{ K}$  and a larger low- $T$  specific heat for near-stoichiometric crystal (#117). This points to another mechanism that contributes to the low- $T$  heat capacity of the UAsSe samples with  $T_C > 111\text{ K}$ . Furthermore, the increase of  $\Theta_D$  only for crystals with  $T_C > 111\text{ K}$  suggests a lattice-related origin of that mechanism [15].

X-ray diffraction measurements, done at room temperature with crystals of very similar  $T_C$  like those discussed here, showed a shrinkage of the unit-cell volume,  $V$ , for those crystals with  $T_C \approx 116\text{ K}$  (see Table 1). Smaller  $V$  as well as higher  $\Theta_D$  values suggest larger bonding forces between the ions forming the crystal lattice of the sample #117 resulting in stronger hybridization strength,  $W$ . The Sommerfeld coefficient is usually directly related to the electronic density of states at the Fermi energy,  $\gamma \sim N(E_F)$ . The latter quantity is inversely proportional to the hybridization strength,  $N(E_F) \sim 1/W$ , i.e. with a decrease of the density of states an increase in the hybridization strength is expected. In the UAsSe case, however, we observe other relationship, i.e. the stronger hybridization (higher  $\Theta_D$ , smaller  $V$ ) is accompanied by larger values of  $N(E_F)$  (larger  $\gamma$ , see Table 1). This suggests a relative shift of the 5f band towards  $E_F$ , which could be responsible for a directly proportional dependence between  $\gamma$  and  $\Theta_D$  in this compound.

The hybridization between 5f and conduction electrons in UAsSe has been demonstrated by the magneto-optical Kerr spectra as well as by ARPES measurements. The latter suggest a d-f character of the hybridization and a position of the 4p band a few eV below  $E_F$ . Furthermore, according to the ARPES experiment, a very narrow 5f band is expected just below  $E_F$  [7,8]. However, the results of the magneto-optical spectroscopy point a position of the 5f band just above  $E_F$  [4,5]. This seeming discrepancy might hint at a rearrangement of the 5f band with respect to  $E_F$ . The driving mechanism responsible for this rearrangement might probably be the slightly different anionic stoichiometry of the UAsSe specimens with different  $T_C$  values. The Se atom has one 4p electron more than As and, therefore, small changes of the As/Se content ratio could be treated like an electron

doping, i.e. a shift of the Fermi level. The low kinetic energy of the 4p band [7,8] allows us to use a rigid-band approximation for  $\text{UAs}_{1-x}\text{Se}_{1+x}$  with  $x \leq 0.06$ .

In fact, the physical properties of UAsSe are very sensitive to slight variations of the As/Se content ratio. The proper stoichiometry of the pnictogen and chalcogen ions is very hard to control during chemical vapor-transport process. Therefore, it is very likely that the specimens prepared in independent laboratories have quite different  $T_C$  values, since the results obtained with them have been different, including variations in the relative position of the 5f band and  $E_F$ .

To conclude, distinct differences in the low- $T$  transport and thermodynamic properties between the UAsSe specimens with slight variations of the As/Se content ratio have been found. In the ferromagnetic state  $\rho(T)$  strongly depends on the sample stoichiometry while in the paramagnetic state  $\rho(T)$  is sample independent. The sample with  $T_C = 116.9\text{ K}$  and almost invisible low- $T$  upturn in  $\rho(T)$  has been considered a near-stoichiometric, only slightly disordered specimen. On the other hand, the sample with the highest RR = 1.27 value can be considered an off-stoichiometry, strongly disordered one. Their different low- $T$  specific heats probably originate from the difference in the hybridization strength between 5f and conduction electrons accompanied by a relative shift of the 5f band with respect to  $E_F$ . A small variation of the anionic stoichiometry is responsible for some kind of electron doping in UAsSe.

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