EVIDENCE FOR A NON-MAGNETIC KONDO EFFECT IN THE STRUCTURALLY DISORDERED UAsSe FERROMAGNET*

T. Cichorek †, R. Michalak, F. Kromer, J. Müller, F. Steglich

Max Planck Institute for Chemical Physics of Solids
01187 Dresden, Germany

A. Wojakowski and Z. Henkie

W. Trzebiatowski Institute of Low Temperature and Structure Research
Polish Academy of Sciences
P.O. Box 1410, 50-950 Wrocław, Poland

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Specific heat and thermal expansion measured along the c-axis are reported for the UAsSe single crystals with $T_C = 101.5$ K, which display the pronounced low-T upturn in the electrical resistivity. Besides the ferromagnetic transition, no additional anomaly has been found that could affect the low-T physics of UAsSe. The investigated ^{77}Se NMR spectra give evidence for a systematic development of the disorder caused by a small change of the sample composition. The appearance of electron-assisted tunneling of the atoms in UAsSe and related compounds is discussed.

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Two Level Systems (TLS's) in disordered solids are believed to be atoms, small groups of atoms, or more complicated clusters, that quantum-mechanically tunnel between two similar energy states separated by a barrier. Experiments show that additional contributions to the thermal properties due to the TLS's are of a very similar size even for quite dissimilar materials. These universal behaviors are dominated by the interaction of the TLS's with phonons rather than with conduction electrons. Moreover, there is no clear experimental evidence for the influence of the TLS's on the electrical

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† On leave from the W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland.

resistivity, $\rho(T)$, [1]. On the other hand, the theoretical calculations predict a rise of $\rho(T)$ with lowering temperature as a result of the electron-assisted tunneling of the atom. This many-body phenomenon can display a non-magnetic analogy to the ordinary Kondo problem [2].

Historically, Cochrane *et al.* [3] were the first who asked whether structural disorder can lead to the existence of a low-energy degree of freedom to which the conduction electrons can couple. However, the non-magnetic $Ni_{75}P_{25}$ alloy that they have investigated has later been recognized as a spin-glass material. Non-magnetic origin of the minimum in the resistivity around 20 K has been observed in the degenerate $Pb_{1-x}Ge_xTe$ semiconductor ($n = 3.4 \times 10^{18}\mathrm{cm}^{-3}$ for $x = 0.006$). It is believed that the random distribution of the Ge atoms induces local strain fields that lift the eightfold degeneracy, plausibly leaving only two levels close in energy at each Ge site and thus giving rise to the TLS's. However, there are some complications because of the ferroelastic transitions, which intervene in the low-T upturn in $\rho(T)$ when the Ge concentration increases (see, *e.g.* [2]).

From the non-magnetic Kondo-problem point of view, the metallic UAsSe system is very interesting (the tetragonal PbFCl-type structure). It undergoes a ferromagnetic phase transition between 96.7 K and 116.9 K for slightly off- (As/Se·0.9) and near-stoichiometric samples, respectively. In spite of the small change of the anionic stoichiometry, the physical properties are strongly sample dependent — especially the electrical resistivity that displays an intriguing upturn in the ferromagnetic state. Its magnitude rapidly increases in a monotonic manner with a smooth decrease of T_C accompanied by a decrease of the As/Se ratio. Above T_C, the $\rho(T)$ behavior of UAsSe has been found to be almost sample independent [4].

In the ordinary Kondo effect, a quenching of the local magnetic moments is essentially based on the antiferromagnetic interactions between itinerant conduction electrons and the magnetic impurity. Since the Kondo screening is extended on the distance of the order of tens of unit cells, the magnetic Kondo effect is unlikely in the ferromagnetically ordered material. (The sizes of the crystallographic and magnetic unit cell are the same in UAsSe.) In addition, the very small magnetoresistance in UAsSe in finite fields up to 13.5 T give an additional experimental evidence for a non-magnetic origin of the negative temperature coefficient of the resistivity, $\beta = 1/\rho \cdot d\rho/dT$, at $T < T_C$ [4].

We do not wish to address here the transport properties of UAsSe, which are widely discussed elsewhere ([5–7] and this issue). In the following, we will mainly focus on the thermodynamic properties of the $T_C = 101.5$ K sample that reveals the pronounced low-T upturn in $\rho(T)$. We will also present the ^{77}Se NMR spectra obtained for specimens with the various As/Se ratios (*i.e.*, different T_C).

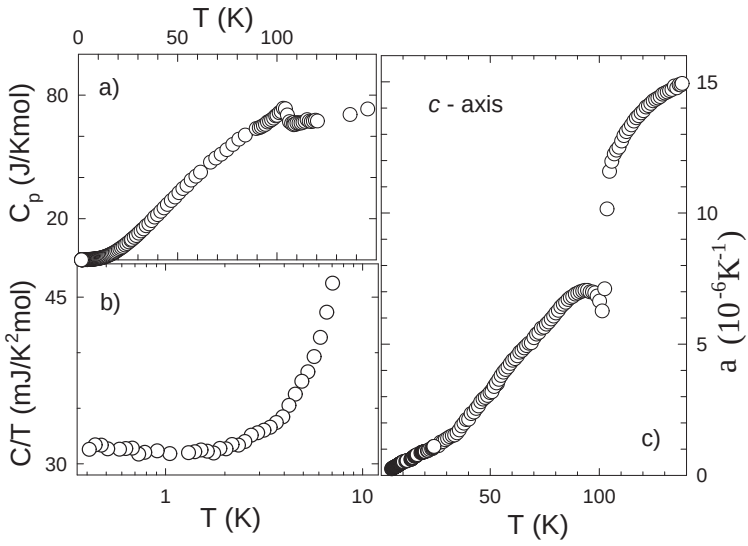

Fig. 1. High- and low-temperature data of specific heat ((a) and (b), respectively) and thermal expansion coefficient, $\alpha(T) = 1/l \cdot dl/dT$, measured along the c-axis (c) for the UAsSe single crystal with $T_{\mathrm{C}} = 101.5\,\mathrm{K}$.

In order to exclude other mechanisms that can also lead to $\beta < 0$, we have investigated the specific heat, $C(T)$, (Fig. 1(a) and 1(b)) and the thermal expansion along the c-axis (Fig. 1(c)). Besides the ferromagnetic transition, no additional anomaly has been found that could affect the low-T properties of UAsSe. Using a capacitive dilatometer with an extremely high relative length-change resolution of $\Delta l/l = 10^{-10}$ we were able to probe the existence of changes in the unit cell volume and/or superstructure formation. Therefore, such phenomena as a structural phase transition or a charge density wave, which could be responsible for $\beta < 0$, should be excluded for UAsSe. Fig. 1(b) reveals the low-T $C(T)/T$ data measured down to 0.4 K. The slight increase of $C(T)/T$ below around 2 K cannot be explained by the "usual" tunneling processes. The linear-in-T contribution from an assembly of the TLS's to the total specific heat is universal and of the order of a one tenth of mJ/Kmol around 1 K, *i.e.*, it is completely screened by the electronic part of $C(T)$ (see, *e.g.*, [1]). At this point of investigation two scenarios based on the disorder appear to be possible: *(i)* an influence of the high-temperature part of the nuclear heat capacities being smeared by the disorder or *(ii)* an action of the electron-assisted tunneling for which large values of $C(T)/T$ are predicted [8]. Although there is not yet unquestionable evidence for the disorder in the UAsSe system, the X-ray as well as the neutron-diffraction

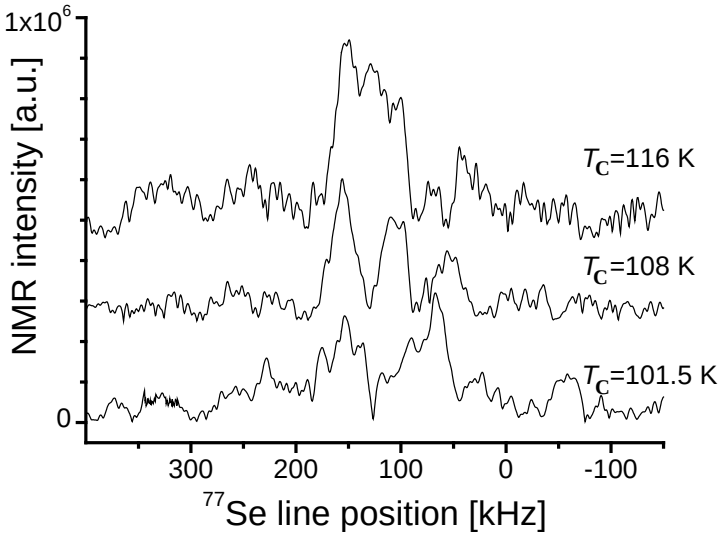

Fig. 2. Room-temperature ^{77}Se NMR spectra in a fixed field of 7 T taken using the spin-echo technique.

experiments clearly hint at such a possibility in the anionic sublattice [9]. In order to establish the existence of the disorder and to investigate any development of it upon decreasing the As/Se ratio, we have performed a ^{77}Se NMR study. The results have been obtained on oriented powders produced by grinding the single crystals of different T_C's: 101.5, 108 and 116 K. For ^{77}Se ($I = 1/2$) one NMR line per crystallographic Se-site is expected. In spite of the poor signal-to-noise ratio, clearly more than one resonance line is observed (Fig. 2) giving evidence for microscopic differences between the samples with various T_C's. For decreasing T_C (decreasing As/Se ratio), the individual line width increases, as does the separation of the lines indicating the developing disorder in UAsSe. Finally, for the sample with $T_C = 101.5$ K, the spectrum is almost completely suppressed. This is probably due to a substantial enhancement of the spin-lattice relaxation time by the large anionic disorder in this sample. In the first interpretation we assume three Se-sites. While one is the unperturbed Se-site, the two others represent: a Se-site that is located in the As-layer and a Se-site in the Se-layer but where As has built into this layer and is part of the first coordination sphere of this Se.

Layers stacked along the c-direction with the sequence: -As-U-Se-Se-U-As- as well as physicochemical affinity between arsenic and selenium quite naturally privilege disorder in the anionic sublattice leaving a well-ordered cationic sublattice [9]. The latter can be, to some degree, treated as a current-carrier reservoir ($5f$ band at the Fermi level [10]). Most probably, the disorder on the microscopic scale in the single-crystalline UAsSe specimens

creates the TLS's centers that interact with the conduction electrons resulting in the non-magnetic Kondo effect at low temperatures. Such a scenario seems to be also realized in other uranium pnictochalcogenides. In spite of the previous work concerning the UPS ferromagnet [11] that reported $\beta > 0$ for all $T < T_C (= 118\,\mathrm{K})$, recent investigations revealed a distinct low-T upturn in $\rho(T)$ for large variety of the UPS single crystals with $T_C \simeq 114\,\mathrm{K}$ [12].

In summary, the investigated thermodynamic properties, $C(T)$ and $\alpha(T)$, of the UAsSe single crystals with $T_C = 101.5\,\mathrm{K}$ support the explanation based on the interaction between the TLS's and the conduction electrons being responsible for the unusual low-T $\rho(T)$ dependence. The ^{77}Se NMR spectra show evidence of the increasing disorder resulting from a smooth change of the sample composition.

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