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Study of the valence state of U ions in quasi-two -dimensional ternary uranium compounds

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The valence states and thermoelectric properties of two Ru-based uranium ternaries, namely U_2Ru_2Sn and U_2RuGa_8, have been studied. Intermediate-valence behaviour manifests itself in broad peaks in the susceptibility, largely negative values of the paramagnetic Curie temperature, and in the occurrence of maxima in the thermoelectric power. At the same time, specific heat data show no transition at low temperatures for both studied compounds. Experimental results are fitted to equations given in the literature relevant to valence fluctuating states. The studied compounds are unique examples of such a state, found for the first time among the huge family of uranium compounds known to be magnetically ordered at low temperatures.

Key words: *mixed valence; magnetic susceptibility; thermoelectric power; actinide intermetallic compounds*

1. Introduction

A fairly large number of Ce, Eu (Sm), and Yb intermetallics have been known for many years to exhibit an intermediate valence (IV) state. Such a state, however, has not been reported up to now for uranium-based intermetallic compounds despite intensive studies of their magnetism and electronic structures for over 50 years. The first example, published recently, turned out to be tetragonal U_2Ru_2Sn, crystallizing in the tetragonal U_3Si_2 type. Its susceptibility was found to exhibit a maximum at about $T_{\max} \approx 170$ K and electrical resistivity (ρ) revealed the formation of a hybridisation gap (or so called pseudo-gap) at the Fermi level (E_F) [1–4]. At higher temperatures, the $d\rho/dT$ derivative becomes negative as for Kondo-like behaviour. These features, among others, classify this compound as a Kondo semiconductor with a narrow gap. U_2Ru_2Sn is so far the only representative of this class in the actinide family. Recent inelastic neutron

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scattering measurements have shown that the observed magnetic response is nearly q-independent, indicating that single-ion type interactions are responsible for the spin gap formation in U_2Ru_2Sn, confirming the presence of a spin gap of the order of 60–70 meV in the electronic structure of this compound [5].

The layered compound $UCoGa_5$ was considered a second candidate exhibiting the IV state among uranium-based ternary intermetallics. The compound crystallizes in a tetragonal $HoCoGa_5$ type structure. The susceptibility of this compound, however, exhibits a maximum at the temperature as high as 650 K [6].

Very recently, we have discovered [7] a third candidate, namely U_2RuGa_8, which joins the still very short list of uranium(IV) compounds. U_2RuGa_8 has also a layered tetragonal structure of the Ho_2CoGa_8 type with the stacking sequence of two layers of UGa_3 and one layer of $RuGa_2$. It is interesting to note that in both types of tetragonal crystal structures, i.e. U_3Si_2 and Ho_2CoGa_8, the closest U–U distances along the a and c axes are almost the same, although their values in each compound are different, i.e. 0.35 and 0.42 nm, respectively. Nevertheless, the magnetic behaviours of both compounds are very similar.

2. Experiment

The tin compound U_2Ru_2Sn and gallides $UCoGa_5$ and U_2RuGa_8 were grown as single crystals by the Czochralski method [2] and so-called self-flux method [7], respectively. Their susceptibility was measured by means of SQUID along two main directions of the tetragonal unit cell, i.e. parallel and perpendicular to the c axis. Thermoelectric power (4.2–300 K) was measured with a steady-state method, also in the two crystallographic directions.

3. Experimental results and fitting procedures

The temperature dependences of magnetic susceptibility measured for U_2Ru_2Sn and U_2RuGa_8 along the two main crystallographic axes a and c are shown in Fig.1. The susceptibility is distinctly anisotropic in both directions and in each case goes through broad maxima at temperatures around 170 and 190 K (U_2Ru_2Sn), and 200 and 220 K (U_2RuGa_8). The upturns in the $\chi(T)$ curves visible at low temperatures are caused by impurities. The susceptibilities measured in these two directions can be fairly well fitted by the interconfiguration fluctuation (ICF) model of Sales and Wohlleben [8] in which a valence fluctuation system is characterized by two energy parameters: E_{ex}, the interconfigurational excitation energy, and by $k_B T_{sf}^*$, where k_B is the Boltzmann constant and T_{sf}^* is the so-called valence fluctuation temperature. This model results in $T_{sf}^* = 180$ K and 500 K for U_2Ru_2Sn, and 320 K and 460 K for U_2RuGa_8 in the two crystallographic directions mentioned above. The energy difference between the corresponding two closest fluctuating states, namely the hybridised $5f^2$ ($6d^1$) and $5f^3$ states (i.e. related to U^{4+} and U^{3+}, respectively), $\Delta E_{ex}/k_B$, is for these two directions less or over 1000 K. In Figure 1, the solid lines are a least squares fit to the expressions given in Ref. [8]. The most important finding characterizing the mixed-valence behaviour is that the susceptibility measured along both directions follows the Curie–Weiss law at temperatures above ~500 K, with the effective magnetic moments of uranium being close to the free ion values for U^{4+} ($5f^2$) and U^{3+} ($5f^3$).

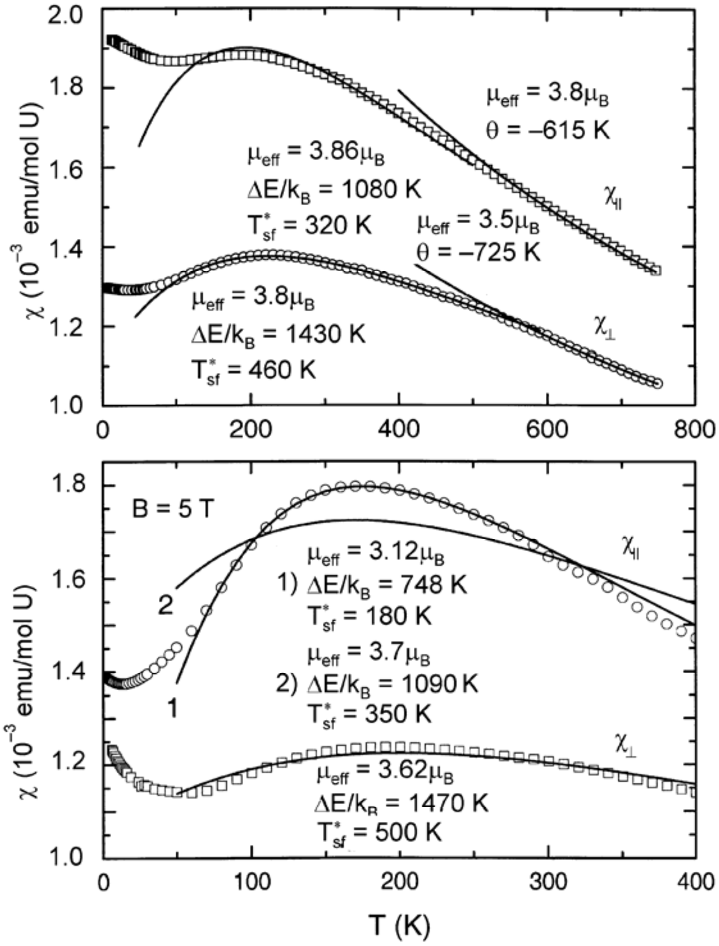

Fig. 1. The Sales–Wohlleben model of intermediate configuration fluctuation (ICF) applied to fitting the experimental temperature dependences of the susceptibilities of U_2Ru_2Sn (a) and U_2RuGa_8 (b), measured parallel and perpendicular to the c axis. The obtained energy parameters E_{ex} and $k_B T^*_{sf}$ are given in the figure

Lawrence et al. [9] have shown that only a single function of a scaled variable T/T^*_{sf} is needed to describe the susceptibility for a broad temperature range, i.e. the squared effective moment $\mu^2_{\text{eff}} \equiv T\chi(T)/C$, where C is the Curie constant of U^{3+}, which satisfies the $\mu^2_{\text{eff}}(T) = f(T/T_s)$ function shown in Fig. 2. T^*_{sf} is defined as the temperature at which the squared effective moment μ^2_{eff} reaches half of the free ion value ($\mu^2(T^*_{sf})$ = 1/2). Thus, it is possible to scale the mixed-valence behaviour of many rare earth compounds on one curve (see, for example, Ref. [10]), including the studied properties of the two uranium representatives along the two main axes of the tetragonal unit cell.

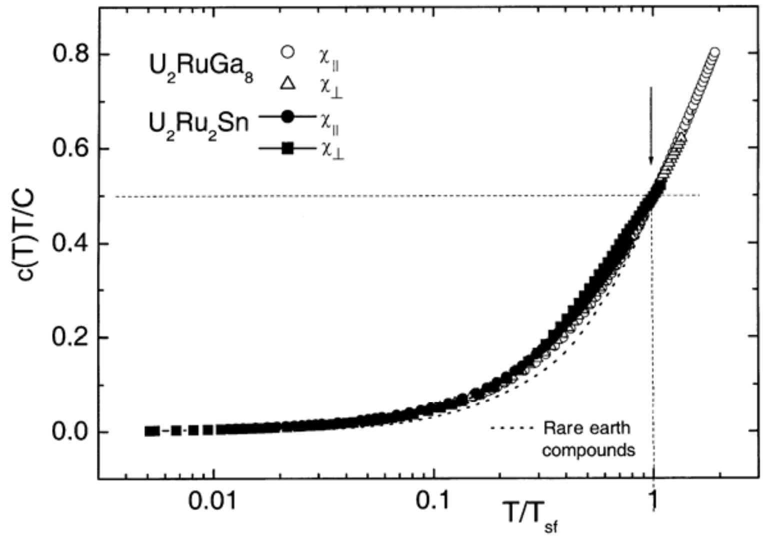

Fig. 2. The scaling scenario in a semi-logarithmic plot for MV rare earths and for the uranium compounds studied in this work

The temperature dependences of electrical resistivity for the current *j* flowing parallel to the *a* and *c* axes are displayed in Refs. [2, 3] and [7] for single crystalline samples of U_2Ru_2Sn and U_2RuGa_8, respectively. Their behaviour confirms once again the mixed valence state of the uranium ions in these compounds. If for the former compound gap formation in the electronic structure is reflected by a low temperature rise in resistivity [2, 3], then for the latter compound a Fermi liquid state at low temperatures is reminiscent to that of many well-known mixed valence lanthanide systems.

The temperature dependences of thermopower *S* for both considered compounds with temperature gradients ∇T, applied along the *a* and *c* axes, have also been studied. For U_2Ru_2Sn, the $S(T)$ curves go through two maxima for both main axes: negative ones at about 20 K and positive ones at high temperatures, where they have different shapes, however, depending on the measured direction. It appears that a fairly sharp maximum occurs at 75 K for the ∇T parallel to *c* axis ($\nabla T||c$), and a very broad one with a maximum at 150 K for the ∇T parallel to *a* axis ($\nabla T||a$). All these data could be fairly well fitted by means of the two-band model [11]. On this basis, energy parameters such as the difference between the electronic levels ($E_f - E_F$) and the width of the 5f electron bands Δ, could be determined. In turn, for U_2RuGa_8, $S(T)$ curves measured along the *a* and *c* axes at first increase with increasing temperature. The curve for $\nabla T || a$ then goes through a broad maximum at 170 K and the curve for $\nabla T || c$ saturates at room temperature. The high temperature variation of $S(T)$, taken as T/S vs. T^2 straight lines for both compounds and for both crystallographic directions, has in turn been fitted by the one band model [12], which has been well-applied in the past to intermediate valence cases of many lanthanide compounds. All these features enabled determination of the energy parameters, which again gives some support for the idea of mixed-valence properties occurring in uranium compounds, until now a phenomenon unknown in this class of materials.

4. Conclusions

Simple intermediate models allowed description of the temperature dependences of magnetic susceptibility and thermoelectric power. Thus, these have provided sufficient proof that both studied ternary compounds can be considered as the first mixed-valence representatives of the family of intermetallic uranium compounds.

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