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Thermoelectric properties of ternary compounds from the U–Fe–Si system

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Abstract

Thermoelectric properties have been studied on ternary compounds from the U–Fe–Si system in term of resistivity and thermopower. Electrical resistivity measurements were carried out in the range 18–300 K for all samples. The thermoelectric power was measured with a thermal gradient of 1 K. Results for $U_3Fe_2Si_7$, U_2FeSi_3, $U_{1.2}Fe_4Si_{9.7}$, $U_2Fe_3Si_5$ and UFe_2Si_2 are shown in this paper.

Keywords: Actinide alloys and compounds; Thermoelectric materials; Transport properties

1. Introduction

The thermoelectric properties of U-based intermetallic compounds show many interesting features which are frequently associated to the formation of a heavy fermion ground state. At high temperatures, they usually behave as normal metals, whereas at low temperatures they often display a positive peak on their thermoelectric power. This anomaly is usually found close to the Kondo temperature [1]. Iron silicide, FeSi, is a small gap semiconductor [2], which shows large thermopower values ($S \sim 500\,\mu V/K$ at 50 K) in combination with low resistivity and thermal conductivity, making it a good candidate for thermoelectric material. It is now commonly thought that the extraordinary thermoelectric properties of heavy fermions and FeSi arise at the transition from the high temperature regime, in which the valence electrons (3d, 4f or 5f) are well localized, to a low temperature regime in which these electrons appears to be more delocalized, leading also to unconventional magnetic properties. Since 10 years, research for new thermoelectric materials is one of the hottest subjects in the field of solid state condensed matter, and one of the most challenging problems to face, as the three parameters which govern the figure of merit ($ZT = S2\sigma T/\kappa$) are dependent each other as a function of the carrier concentration [3]. In particular, σ and κ generally vary in a reciprocal way making an improvement of the figure of merit a tricky task. Therefore novel approaches, including investigation of new classes of materials is highly desirable.

In the frame of this project, a comprehensive investigation of the ternary systems combining iron, silicon and uranium has been initiated. Our experimental procedure comprise the assessment of the phase relationships at a given temperature, and the investigation of the electronic properties (magnetic and transport properties) of the ternary phases. At the beginning of our study, numerous investigations dealing with the crystal-chemistry and physical properties of ternary uranium iron silicides were already available. Nine ternary compounds were known: $U_3Fe_2Si_7$ ($U_3Fe_2Si_7$-type), U_2FeSi_3 (AlB_2-type), and $U_{1.2}Fe_4Si_{9.7}$ ($Er_{1.2}Fe_4Si_{9.7}$-type) being classified as heavy fermion compounds [4–6]; UFe_2Si_2 ($BaAl_4$-type) exhibiting Kondo behaviour [7]; UFeSi (TiNiSi-type) displaying spin fluctuations [8]; $U_2Fe_3Si_5$ ($Lu_2Co_3Si_5$-type) showing a weakly paramagnetic temperature-independent behaviour [9]; and U_2Fe_3Si ($MgZn_2$-type) with unknown physical properties. Magnetic ordering, with ferromagnetic transitions have been only observed for $U_2Fe_{13}Si_4$ (Th_2Ni_{17}-type) and $UFe_{10}Si_2$ ($ThMn_{12}$-type), with Curie temperatures of 495 K and 650 K, respectively [10]. Experimental data about thermoelectric power are missing. Here we present the electrical resistivity and thermopower measurements of the non-magnetically ordered $U_3Fe_2Si_7$, U_2FeSi_3, $U_{1.2}Fe_4Si_{9.7}$, UFe_2Si_2 and $U_2Fe_3Si_5$ ternary compounds.

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2. Experimental

Samples (each weighing ~0.5 g) were prepared by melting the elemental components in an arc furnace, under high purity argon. They were then introduced in evacuated quartz tubes which were sealed under residual atmosphere of argon and annealed at 900 °C for 10 days. Their quality was checked by X-ray powder diffraction techniques, using an Inel CPS 120 diffractometer working with Co Kα radiation, and by metallographic analyses carried out on thoroughly polished surfaces, using a Jeol JSM 6400 scanning electron microscope (SEM). Finally, the composition of the phases was established by energy dispersive X-ray spectroscopy (EDS) with an Oxford Link-Isis Si/Li analyzer.

The electrical resistivity was measured in a closed-cycle refrigerator in the 18–300 K temperature range using the four-probe ac method. The thermoelectric power was measured relative to gold by a slow ac technique (10^{-2} Hz), with a thermal gradient of 1 K, in an home-made apparatus similar to the one previously described by Chaikin et al. [11].

3. Results

The temperature dependence of the electrical resistivity of $U_3Fe_2Si_7$, U_2FeSi_3, $U_{1.2}Fe_4Si_{9.7}$, UFe_2Si_2 and $U_2Fe_3Si_5$ is shown in Fig. 1. Our data compare well the previous resistivity measurements [4–6]. With the exception of $U_2Fe_3Si_5$, the curves are nearly flat and featureless. The gentle slope of the resistivity of $U_3Fe_2Si_7$ and U_2FeSi_3, with values of about 1–6 μΩ m, indicates metallic behaviour. Only at temperatures below 30 K, the resistivity of $U_3Fe_2Si_7$ displays a more negative curvature. $U_{1.2}Fe_4Si_{9.7}$ has the highest resistivity values, the curve slightly increasing with decreasing temperature. This type of behaviour, which is reminiscent of semiconductors, suggests that the compound is more appropriately classified as a semimetal. However, such behaviour can also reflect the disorder of the structure [6]. The small change from the ln T dependence of the resistivity of $U_2Fe_3Si_5$ below 80 K, points to a weak Kondo behaviour in this compound. In agreement with the previous work [7] UFe_2Si_2 exhibits a typical metallic behaviour above 20 K.

Thermopower data of $U_3Fe_2Si_7$, U_2FeSi_3, $U_{1.2}Fe_4Si_{9.7}$, UFe_2Si_2 and $U_2Fe_3Si_5$ are depicted in Fig. 2. All samples have modest values of few μV/K in the temperature range 20–300 K.

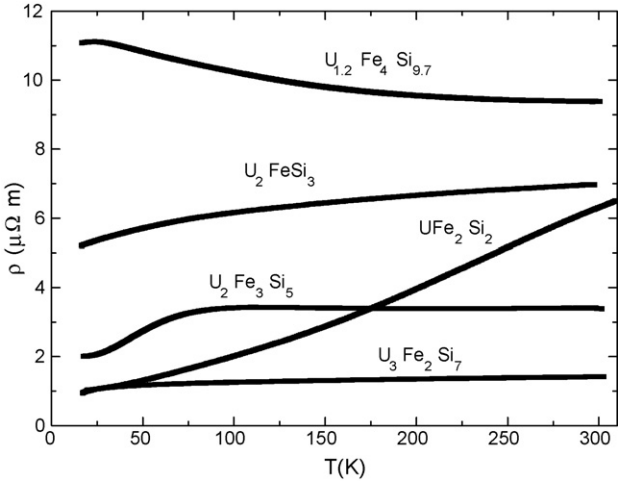

Fig. 1. Resistivity measurement of U–Fe–Si ternary compounds.

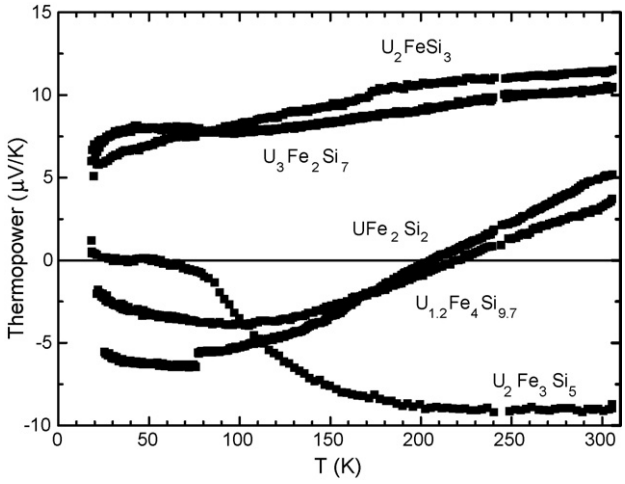

Fig. 2. Thermopower measurement of U–Fe–Si ternary compounds.

At temperatures above 150 K, the thermopower of $U_3Fe_2Si_7$, U_2FeSi_3, $U_{1.2}Fe_4Si_{9.7}$ and UFe_2Si_2 shows linear temperature dependences, as expected for normal metals. For $U_3Fe_2Si_7$ and U_2FeSi_3, the thermopower is positive in the whole temperature range, whereas for $U_{1.2}Fe_4Si_{9.7}$ and UFe_2Si_2 it changes from positive to negative at about 200–220 K. For these last two compounds, the thermopower deviates from linearity at temperatures below 150 K, to reach a shallow minimum and smoothly rise at lower temperature. In the case of $U_3Fe_2Si_7$ the thermopower decreases below 30 K, confirming the trend already observed in the electrical resistivity. Such low temperature behaviour may be associated to a weak Kondo scattering. At temperatures above 200 K, the thermopower of $U_2Fe_3Si_5$ is almost temperature-independent with negative numerical values, it decreases slowly with decreasing temperature and then saturates below about 80 K to a value close to zero, in agreement with the electrical resistivity measurements. This shape of $S(T)$ is often observed for Ce- or U-based intermetallic compounds and may illustrate the competing interaction present in the heavy fermion systems and the sensitivity of S to details of the band structure [1,12].

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References

[1] A.K. Bhattacharjee, B. Coqblin, Phys. Rev. B 13 (1976) 3441.
[2] V. Borisenko (Ed.), Semiconducting Silicides, Springer, Berlin, 2000.
[3] R.R. Heikes, R.W. Ure Jr., Thermoelectricity: Science and Engineering, Interscience Publishers, New York, London, 1961.
[4] F.G. Aliev, L.G. Aksel'rud, V. Kozyr'kov, V.V. Moshchalkov, Fizika Tverdogo Tela 30 (5) (1988) 1278.
[5] N. Takeda, M. Ishikawa, J. Phys. Soc. Jpn. 67 (3) (1998) 1062.
[6] S. Noguchi, K. Okuda, T. Adachi, Y. Haga, E. Yamamoto, Y. Onuki, J. Phys. Soc. Jpn. 66 (1997) 2572.
[7] A. Szytula, M. Slaski, B. Dunlap, Z. Sungaila, A. Umezawa, J. Magn. Magn. Mater. 75 (1988) 71.

[8] A.V. Andreev, F. Honda, V. Sechovsky, M. Divis, N. Izmaylov, O. Chernyavski, Y. Homma, Y. Shiokawa, J. Alloys Compd. 335 (2002) 91.
[9] E. Hickey, B. Chevalier, P. Gravereau, J. Etourneau, J. Magn. Magn. Mater. 90–91 (1990) 501.
[10] T. Berlureau, B. Chevalier, L. Fournes, J. Etourneau, Mater. Lett. 9 (1) (1989) 21.
[11] P.M. Chaikin, J.F. Kwak, Rev. Sci. Instrum. 46 (1975) 218.
[12] A. Amato, D. Jaccard, J. Sierro, F. Lapierre, P. Haen, P. Lejay, J. Flouquet, J. Magn. Magn. Mater. 76–77 (1988) 263.