Journal of Nuclear Materials 389 (2009) 98–100

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Thermoelectric power studies of ferromagnet $U_2ScB_6C_3$

V.H. Tran [a,*], W. Miiller [a], P. Rogl [b]

[a] Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland
[b] Institute of Physical Chemistry, University of Vienna, Währingerstr. 42, A-1090 Wien, Austria

A B S T R A C T

The thermoelectric power (*TEP*) of a ferromagnet $U_2ScB_6C_3$ ($T_C = 61$ K) has been measured in the temperature range 5–300 K. The *TEP* is positive over the whole measured temperature range and reaches a relatively large value at room temperature of 29 μV/K. Below 30 K and above 200 K the *TEP* follows a straight line $S(T) \sim AT$, with slope of 0.23 and 0.085 $\mu V/K^2$, respectively. The change in the slope can be explained by the electron–phonon interaction renormalization effects or spin-reorientation associated with a change in the electronic structure. Analysing the temperature dependence of the ratio $[S(T)/T]/[S_{300\,K}/300]$ and taking into account the specific heat data, we suggest that spin fluctuations are another important factor in determining the thermoelectric power behaviour of $U_2ScB_6C_3$.

1. Introduction

Due to a high absorption cross-section, boron and its alloys are commonly used as shielding materials for thermal neutrons. On the other hand, uranium carbides are very promising fuels for nuclear reactors of generation IV. These reasons have motivated the study of the ternary system U–B–C [1], leading to discovery of the boron-carbide UB_2C phase. It was found that this phase exists in two modifications [1]. The low-temperature form called α-UB_2C crystallizes in the orthorhombic space group *Pmma* [2], whereas the high-temperature form, called β-UB_2C, adopts the rhombohedral ThB_2C-type structure (space group $R\bar{3}m$) [3]. The magnetic properties of these compounds are completely different. The α-form is a temperature independent paramagnet, whilst the β-form is ferromagnetic with $T_C \sim 74.5$ K [4,5].

The Sc-substitution for U in UB_2C results in a new quaternary boron-carbide $U_2ScB_6C_3$ [6]. The compound adopts a unique structure type with space group P6/*mmm*, being an ordered variant of the rhombohedral ThB_2C-type structure. The lattice relation to the structure type of ThB_2C (isotype β-UB_2C) is as follows: $a(U_2ScB_6C_3) = a(\beta\text{-}UB_2C)$ and $c(U_2ScB_6C_3) = 1/3c(\beta\text{-}UB_2C)$. In spite of this relationship, distinct differences exist in the unit cells. The ThB_2C structure is built from three puckered metal layers per unit cell while in $U_2ScB_6C_3$ both the non-metal and metal layers are perfectly planar.

The very recent investigation on $U_2ScB_6C_3$ [7] revealed that the substitution of one U atom by one Sc atom in UB_2C, not only decreases Curie temperature, from 74.5 to 61 K, but also results in anomalous behaviour of electrical resistivity $\rho(T)$ and specific heat properties. $U_2ScB_6C_3$ exhibits an enhancement in the electronic specific heat ($C_p/T \sim 40$ mJ mol^{-1} K^{-2} at 2 K) and it is regarded as a strongly correlated electron material. At higher temperatures ($T > 150$ K) the susceptibility is described by a modified Curie–Weiss law and the measured effective moment of 2.04 μ_B/U, compared to 1.45 μ_B/U in β-UB_2C indicates a higher degree of localization of 5f-electrons in $U_2ScB_6C_3$. The temperature dependence of the magnetization at low temperatures is characteristic for spin-wave systems. The analysis of isotherms, in addition to the ferromagnetic transition at 61 K, indicates an anomaly around $T^* \sim 45$ K, probably of spin-reorienation origin. Subsequent specific heat measurement showing some broad maximum between T^* and T_C could support the magnetic nature of the anomaly at T^*. The $\rho(T)$-curve of $U_2ScB_6C_3$ is of typical behaviour for metallic ferromagnets, i.e., the $\rho(T)$ increases with increasing temperature and exhibits a knee at T_C. The metallic properties of $U_2ScB_6C_3$ may be supported further by electronic band calculations based on the full-potential linear augmented plane wave approach. The existence of the anomaly at T^* can be evidenced by the resistivity measurement as a maximum in the temperature derivative $d\rho(T)/dT$. The observed large residual resistivity of ~430 μΩ cm and small residual resistivity ratio in $U_2ScB_6C_3$ may have different origins. In U-based intermetallics, Kondo effect and/or electron localization frequently give a rise to the resistivity. For $U_2ScB_6C_3$, the influence of separated layers of the non-metal atoms and metal atoms, and as well as some microcracks increasing the resistivity values cannot be excluded.

We may recall that β-UB_2C, in spite of its metallic nature, exhibits a remarkable thermoelectric power (S), *TEP* at room temperature as large as 22.5 μV/K [5]. Thus, it is highly desired to study its related compounds in the context of underlying physics of the enhanced *TEP* in intermetallics. Compared to β-UB_2C, the $U_2ScB_6C_3$

---

* Corresponding author.
E-mail address: V.H.Tran@int.pan.wroc.pl (V.H. Tran).

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.01.032

compound of the layer-type structure is expected to have better thermoelectric power figure of merit $Z = \frac{S^2}{\rho\kappa}$, where ρ is the electrical resistivity and κ is the thermal conductivity, because the layer-type structure of the compound should decrease the thermal conductivity. Besides, $U_2ScB_6C_3$ has enhanced electronic specific heat coefficient. As a consequence, charge carriers may have large effective mass at low temperatures, which in turn usually leads to large values of the thermoelectric power. Thus, the subject of this work is to study the thermoelectric power property of $U_2ScB_6C_3$ and to compare it to that of β-UB_2C.

2. Experimental details

Samples used in this work are polycrystals prepared by arc-melting technique which was described elsewhere [3,6]. We performed powder X-ray diffraction, SEM and EDX to check quality of the samples. Electrical resistivity was measured on bar shaped samples applying a standard 4-probe a.c. technique at temperatures down to 2 K. Thermoelectric power was measured with a steady-state method between 5 and 300 K. Applied temperature gradient of about 1 K across the sample length was measured by a pair of fine Au(Fe 0.07%)/Chromel thermocouples. The accuracy of the measurement was estimated to be about ±1 μV/K.

3. Results

Fig. 1 shows temperature dependence of the thermoelectric power of $U_2ScB_6C_3$. The compound has positive *TEP* values over the whole measured temperature range. At high temperatures, the *TEP* is nearly linear in *T* with the slope $\sim$0.085 μV/K^2. This observation may suggest that contribution from thermal diffusion of carriers to the total thermopower is dominating compared to phonon-drag contribution. One should note that the magnitude of *TEP* attains a value of 29 μV/K at room temperature, thus higher than that associated with free electrons like in ordinary metals (*TEP* of Cu and Pb is of about few μV/K at room temperature).

At low temperatures, the $S(T)$-curve can also be described by a straight line. Therefore, there is no indication of either phonon-drag peak or magnon-drag anomaly in the $S(T)$ dependence of $U_2ScB_6C_3$. This means that these contributions are relatively minor compared to the thermopower due to thermal diffusion of carriers. The latter contribution is given as: $S(T) = \frac{\pi^2 k_B^2}{3e}\frac{\partial\sigma(E)}{\sigma(E)\partial E}\Big|_{E_F}$, where k_B is the Boltzmann constant and $\sigma(E)$ is the energy dependence of dc conductivity [8]. At low temperatures and in a single parabolic band system, it approximates to the Mott formula: $S(T) = \frac{\pi^2 k_B^2}{3eE_F}T$, where E_F is the Fermi energy relative to the maximum of the density of states [8,9]. Analysing the low-temperature *TEP* data, we obtained a slope of 0.23 μV/K^2, corresponding to energy $E_F = 0.106$ eV. This value agrees very well with the theoretical value of 0.15 eV (see the inset), which is obtained with employing a full-potential linear augmented plane wave approach [7].

Obviously, in addition to the diffusion thermopower, there are other contributions, which give a rise to a non-linear temperature dependence of $S(T)$. Besides phonon-drag and magnon-drag contributions mentioned above, one considers contribution due to renormalization effects of electron–phonon interaction. According to Kaiser [10], electron–phonon renormalization would lead to an enhanced thermopower by a parameter $\lambda(T)$, and then the measured thermopower can be expressed as: $S(T) = S_b(1 + \lambda(T))$, where S_b is the diffusion thermopower without renormalization effects. As we have shown above, at high temperature the diffusion thermopower is linear in *T*, so the ratio $[S(T)/T]/[S_{300\,K}/300\ K]$ would give a measure of $\lambda(T)$.

We plot in Fig. 2(a) the temperature dependence of $[S(T)/T]/[S_{300\,K}/300]$ for $U_2ScB_6C_3$. The magnitude of the ratio $[S(T)/T]/[S_{300\,K}/300\ K]$ increases as temperature lowers down and shows a broad maximum around 35 K. The appearance of this maximum reflects unusual behaviour of *TEP* of $U_2ScB_6C_3$, since some change due to a spin reorientation was observed at somehow higher

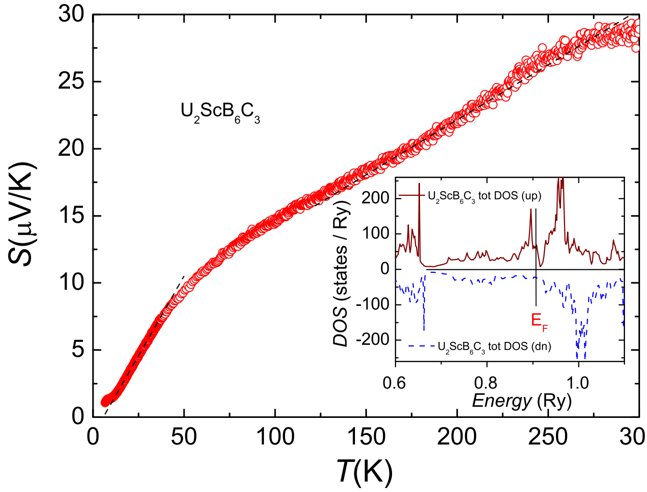

Fig. 1. Temperature dependence of the thermoelectric power of $U_2ScB_6C_3$. The dashed lines are guides for the eye. The inset shows density of states calculated with FP-LAPW approach [7].

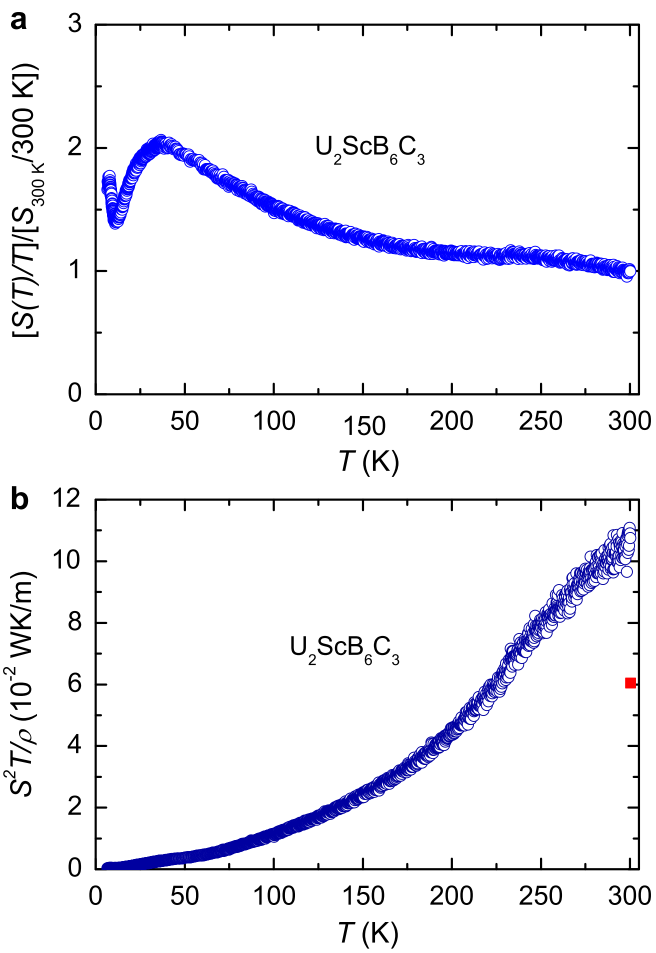

Fig. 2. Temperature dependence of (a) the ratio $[S(T)/T]/[S_{300\,K}/300\ K]$ and (b) of thermoelectric power factor (FP) S^2T/ρ of $U_2ScB_6C_3$. The FP value of β-UB_2C at 300 K is shown as closed square.

temperature, i.e., ~45 K in other physical properties like magnetization, resistivity and specific heat [7]. If the spin reorientation is responsible for this maximum, then some change in the electronic structure of $U_2ScB_6C_3$ must occur. Interestingly, below 10 K we observe increase in $[S(T)/T]/[S_{300\,K}/300\,K]$, suggesting additional mechanism other than electron–phonon interaction or spin-reorientation. We may recall that from the specific heat data $U_2ScB_6C_3$ has been reported to have strong spin fluctuations. A large electron mass-enhancement calculated from the electronic specific heat coefficients $\lambda = \frac{\gamma_{exp}}{\gamma_{theo}} - 1$ of 4.1 was already estimated [7].

To discuss the transport properties of $U_2ScB_6C_3$ in the context of thermoelectric materials, we plot in Fig. 2(b) the thermoelectric power factor (PF) S^2T/ρ as a function of temperature. At room temperature the power factor reaches a large value of 0.1 W/Km. This PF is much larger than that observed in β-UB_2C (0.06 W/Km). However, neither of them attains the value exhibited by the best thermoelectric materials based on Bi_2Te_3 (~1.7 W/Km) [11].

4. Conclusions

A comparative study on crystallographic, magnetic and thermoelectric power properties has been performed for β-UB_2C and $U_2ScB_6C_3$. Both compounds crystallize in a hexagonal unit cell with a lattice relation close to the structure type of ThB_2C. The published data by us indicate that the substitution of one U atom by one Sc atom in UB_2C, not only decreases Curie temperature, from 74.5 to 61 K, but also results in anomalous behaviour, such as an increase in the Sommerfeld ratio at 2 K, the disappearance of the specific heat hump near 37 K in β-UB_2C and appearance of spin-reorientation at 45 K in $U_2ScB_6C_3$. Here, we demonstrate that this substitution causes an enhancement of *TEP* at high temperatures for $U_2ScB_6C_3$. To explain these changes one considers electronic structure of these compounds. There is considerable increase in conduction electron density in the Sc-based compound compared to that of β-UB_2C. Taking into account the specific heat data previously reported [5,7], the electronic density of states at the Femi level $N(E_F)$ can be evaluated to be 17.4 states/eV at. and 14.7 states/eV at. for $U_2ScB_6C_3$ and β-UB_2C, respectively. As a consequence, the DOS position in respect to the Fermi energy is expected to be changed, and the derivative $dN(E_F)/dE$ determined the *TEP* in $U_2ScB_6C_3$ is certainly higher than that for β-UB_2C. We have shown that the thermoelectric power of $U_2ScB_6C_3$ can be attributed to thermal diffusion of carriers, electron–phonon interaction renormalization effects, spin-reorientation and spin fluctuations. These three latter effects have found to give a rise to thermopower value and to cause change in the slopes of $S(T)$-curve around T^*. Though it has a relatively large thermopower at room temperature, the PF is lower by an order of magnitude than that of Bi_2Te_3.

Acknowledgements

The author V.H.T. would like to thank financial support from The Ministry of Science and Higher Education under Grant no. N202 082 31/0449 and support from COST Action P16 Emergent Behaviour in Correlated Matter (ECOM) for attending the STTNM08 conference attending.

References

[1] P. Rogl, J. Bauer, J. Debuigne, J. Nucl. Mater. 165 (1989) 74.
[2] P. Rogl, P. Fischer, J. Solid State Chem. 90 (1991) 285.
[3] P. Rogl, P. Fischer, J. Solid State Chem. 78 (1989) 294.
[4] P. Rogl, B. Rupp, I. Felner, P. Fischer, J. Solid State Chem. 104 (1993) 377.
[5] V.H. Tran, P. Rogl, G. André, F. Bourée, J. Phys.: Condens. Matter 18 (2006) 703.
[6] T. Mori, T. Tanaka, P. Rogl, Crystal structure and properties of quaternary actinoid boron carbides, $Th_2ScB_6C_3$ and $U_2ScB_6C_3$, in: Proceedings of the International Conference on Actinoids, Japan, J. Nucl. Sci. Technol., 2002 (Suppl. 3), p. 122.
[7] V.H. Tran, P. Rogl, T. Mori, H. Ripplinger, K. Schwarz, Chem. Mater. 20 (2008) 5643.
[8] F.J. Blatt, P.A. Schroeder, C.L. Foiles (Eds.), Thermoelectric Power of Metals, Plenum, New York, 1976.
[9] N.F. Mott, Conduction in Non-crystalline Materials, second ed., Clarendon, Oxford, 1993.
[10] A.B. Kaiser, Phys. Rev. B 35 (1987) 4677.
[11] G.S. Nolas, J.W. Sharp, H.J. Goldsmid, Thermoelectrics: Basic Principles and New Materials Developments, Springer-Verlag, Heidelberg, 2001.