Philosophical Magazine
Vol. ??, No. ?, Month?? 2008, 1–4

Taylor & Francis
Taylor & Francis Group

Thermodynamics and superconductivity of the $Th_7(Fe, Ru, Os, Co, Rh, Ir)_3$ system

J.L. Smith[a], J.C. Lashley[a]*, H.M. Volz[a], R.A. Fisher[a] and P.S. Riseborough[b]

[a]*Los Alamos National Laboratory, Los Alamos, NM 87545, USA;* [b]*Department of Physics, Temple University, Philadelphia, PA 19122, USA*

(*Received 27 June 2008; final version received 2 August 2008*)

Expanding the temperature range of previous specific-heat measurements on the $Th_7(Fe, Ru, Os, Co, Rh, Ir)_3$ system, we measure the effect of transition-metal substitution on total entropy ($S^{\circ}_{298\,K}$), electronic specific heat (γ), and Debye temperature (Θ_D). In addition we measure the pressure dependence, up to 10 kbar, of the superconducting transition.

Keywords: ▮▮▮▮

1. Introduction

Magnetism and superconductivity can arise with many patterns. The elements iron, cerium, plutonium, and their neighbours sit on the edge between superconductivity and magnetism, that is, between itinerant and localized electron behaviour [1]. For example, uranium behaves like a hexavalent transition metal when alloyed in titanium and raises the T_c [2], while iron in titanium also looks non-magnetic and raises T_c [3]. Itinerant 5*f*-electrons lower their energies by causing Peierls-like distortions [4] or by mixing with *d*-electrons on the border of localization. This mixing leads to the lowest-symmetry structures in the periodic table, except for thorium which is fcc and rarely shows its *f*-electron character. Johansson et al. have argued that thorium's fcc crystal structure should be expected to be a hexagonal closed packed (hcp) metal like other group IVA elements, and it is therefore showing its *f*-electron character [5].

Matthias et al. reported that $Th_7(Fe, Os, Co, Rh, Ir, Ni)_3$ were all superconducting between 1.5 and 2.2 K [6,7]. This result suggested the possibility of the coexistence of magnetism and superconductivity arising from the interaction of localized *f* moments and additional band magnetism moments. However low-temperature specific-heat and ac-susceptibility measurements showed that Th_7Fe_3 and related compounds in that structure are quite ordinary BCS superconductors [8–10]. Here we extend the temperature range of previous measurements to higher temperatures to evaluate the specific heat of the $Th_7(Fe, Ru, Os, Co, Rh, Ir)_3$ system. In addition we measure the pressure dependence of the superconducting transition in Th_7Fe_3. It was determined that the sample quality was

*Corresponding author. Email: j.lash@lanl.gov

ISSN 1478–6435 print/ISSN 1478–6443 online

DOI: 10.1080/14786430802389197
http://www.informaworld.com

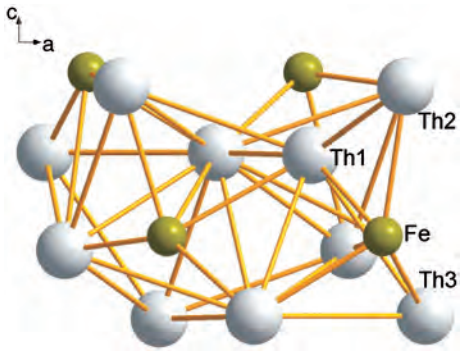

Figure 1. Hexagonal structure of the Th_7M_3 structure projected along the *b*-axis. The three inequivalent Th positions are labelled.

higher, based on residual resistivity ratios (RRR), and the superconducting transition temperatures did not change appreciably.

2. Experiment

The samples were prepared by arc melting pre-weighed elements in Zr-gettered argon at least eight times with flipping between the melts. Weight losses were negligible. The thorium metal was either crystal bar from vapour transport or metal from an unknown source that had been arc melted in small pieces (about a gram) until weight losses from melting ceased. The other elements, Fe, Co, Ni, Rh, Os, and Ir were at least 5–9's pure. Samples were wrapped in tantalum foil, sealed in quartz with some helium gas, and heated in a furnace. First the samples were homogenized below any known nearby eutectic temperature (invariant reaction) for several days, and second they were heated close to the melting point for several more days. Laboratory X-ray powder diffraction (sealed tube, Cu K_α radiation) confirmed that no other phases were present. A GSAS full-pattern Rietveld refinement [11] determined the lattice parameters of Th_7Fe_3 to be $a = 9.8281(5)$ and $c = 6.2153(4)$. The heat-capacity measurements were made by a thermal-relaxation technique [12], and the pressure measurements were made by a four-terminal technique in a pressure cell designed to reach pressures of 30 kbar [13].

3. Results and discussion

The symmetry of the A_7B_3 system (A = La, Th) (B = Fe, Ru, Os, Co, Rh, Ir, Ni) is hexagonal belonging to the P63mc (no. 186) space group. The iron atoms occupy 6*c* positions $(x, -x, z)$, while there are three separate thorium atom positions: one at the 2*b* site $(1/3, 2/3, z)$ and the other two at different 6*c* sites as shown in Figure 1.

Figure 2 is a plot of $(C - \gamma T)$ vs. T to 300 K. The γT electronic contribution was evaluated from a preliminary fit from $2\,K < T < 15\,K$ to the expression $C = \gamma T + \beta_3 T^3 + \beta_5 T^5$, where the lattice contribution was represented by two terms of the harmonic-lattice approximation. A fit of the lattice heat capacity, $C_{lat} = (C - \gamma T)$, was made using Debye (acoustic) and Einstein (optical) modes – the Born–von Karman model.

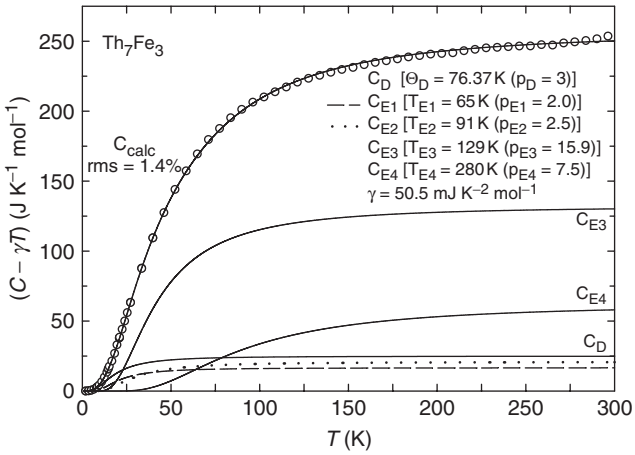

Figure 2. $(C - \gamma T)$ vs. T for Th_7Fe_3 to 300 K. Debye (for acoustic) and four Einstein (for optical) functions were used to fit the lattice data. Colour-coded curves represent the contributions of the various components with their parameters shown in the figure. The characteristic Debye temperature is Θ_D and the Einstein temperatures are T_E.

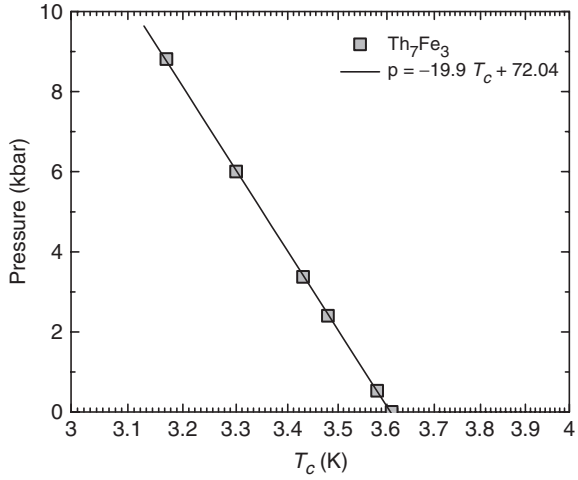

Figure 3. Pressure dependence of the superconducting transition in Th_7Fe_3 up to 10 kbar. A linear fit characterizes the data over the full range of pressure.

Th_7Fe_3 has 30 vibration modes – three acoustic and 27 optical. The acoustic modes are represented by the Debye specific heat and the optical modes by the Einstein specific heat function. The Debye temperature and Einstein temperatures, and their modes, used for the fit are given in the figure. Colour-coded curves represent contributions of the various components and their sum. The number of modes used in the fit was 30.9 instead of 30, where the excess 0.9 mode is probably associated with dilation (the measurements were made at constant pressure) and anharmonic contributions. Overall the fit is a very good

Table 1. Tabulated thermodynamic data and residual resistivity rations (RRR) for the Th_7M_3 series.

M	γ (mJ $K^{-1}mol^{-1}$)	Θ_D (K)	$S^{\circ}_{298\,K}$(J $K^{-1}mol^{-1}$)	RRR	T_c(K) onset
Fe	50.5	76.3	481	14.7	2.26
Ru	36.3	82.3	478	2	n.s.
Os	35.2	81.4	483	5	2.92
Co	43.2	82.9	438	7.6	2.59
Rh	42.9	81.8	439	2.5	2.41
Ir	39.8	81.4	494	–	2.96

representation of C_{lat}. Going down the VIII and VIIII a families, the γ values decrease monotonically while the Debye temperatures remain virtually unchanged. The unchanging Debye temperatures seem to be mirrored by the total entropy which also do not appreciably vary through the series.

The pressure dependence, up to 10 kbar, is shown in Figure 3. One sees that the transition temperature decreases linearly dT/dp -0.04 K $kbar^{-1}$, within experimental error, with pressure. In Table 1 we summarize our results. We set out with better samples to see if we could find anything in this system that was new or exciting, and what we have that is new is the pressure dependence of T_c and the thermodynamic variables.

In conclusion, we have confirmed earlier work using better samples, measured the entropies at room temperature, measured the pressure dependence of the transition, and thank Peter Weinberger for a lifetime of encouragement.

Acknowledgements

This work was performed under the auspices of the United States Department of Energy.

References

[1] J.L. Smith and E.A. Kmetko, J. Less-Common Metals 90 (1983) p.83.
[2] V.O. Struebing, H.H. Hill and J.L. Smith, Solid State Comm. 25 (1978) p.1041.
[3] B. Matthias, V.B. Compton and H. Suhl, Phys. Rev. 115 (1959) p.1597.
[4] R.E. Peierls, *Quantum Theory of Solids*, Oxford University Press, Oxford, 1955.
[5] B. Johansson, R. Ahuja and O. Eriksson, Phys. Rev. Lett. 75 (1995) p.280.
[6] B.T. Matthias, V.B. Compton and E. Corenzwit, J. Phys. Chem. Solids 19 (1961) p.130.
[7] B.T. Matthias, T.H. Geballe and V.B. Compton, Rev. Mod. Phys. 35 (1963) p.1.
[8] M. Noack, F. Laabs and J. Smith, Z. Metal. 81 (1990) p.239.
[9] J.G. Sereni, G.L. Nieva and J.G. Huber, Physica C 230 (1994) p.159.
[10] P. Pedrazzini, G. Schmerber and M. Gómez Berisso, Physica C 336 (2000) p.10.
[11] A.C. Larson and R.B. Von Dreele, *General Structure Analysis System (GSAS)*, Los Alamos National Laboratory, Report LA-UR 86-748, 1994.
[12] J.C. Lashley et al., Cryogenics 43 (2003) p.369.
[13] EasyLab Technologies Limited, Egham Surrey, UK; www.easyLab.co.uk