Magnetic and thermodynamic properties of $Ce_{23}Ru_7Mg_4$ compound

J C Debnath[1], A M Strydom[1] , O Niehaus[2] and R Pöttgen[2]

[1]Highly Correlated Matter Research Group, Department of Physics, University of Johannesburg, South Africa.
[2]Institut für Anorganische und Analytische Chemie, Universität Münster, Germany.

Author e-mail address: jdebnath@uj.ac.za

Abstract. The magnetic susceptibility and heat capacity of the novel compound $Ce_{23}Ru_7Mg_4$ have been studied above room temperature to low temperature range and in the applied magnetic field up to 7 T. This compound crystallizes with the hexagonal non-centrosymmetric $Pr_{23}Ir_7Mg_4$-type structure, with space group $P6_3mc$. The structure is built up from complex three dimensional networks of edge and corner-sharing RE_6Ru trigonal prisms. The magnetic susceptibility and specific heat both exhibit a distinct anomaly at about ~2 K which most probably suggests a paramagnetic to antiferromagnetic phase transition. The magnetic susceptibility revealed a magnetic moment μ_{eff} = 2.24 μ_B/Ce which is close to the value for cerium in pure Ce metal (μ_{eff} = 2.54 μ_B), indicating a presence of well localized magnetic moments carried by the stable Ce^{3+} ions but with significant deviation from full moment. The magnitude of the electronic specific heat coefficient γ = 127 mJ/Ce-mol K^2 suggests correlated electron behavior in this compound.

1. Introduction

Complex metal alloys have been shown to offer new possibilities in developing high efficiency thermoelectric material [1]. Among the correlated electron class of magnetic systems, the enhanced thermoelectric power characteristic of Kondo metals offers a distinct advantage in gaining thermoelectric efficiency. In recent years, the rare earth (RE)–transition metal (T)–magnesium systems has been studied a few with respect to phase analyses, crystal structures, and chemical bonding as well as magnetic and mechanical properties. The rare earth (RE) metal rich $RE_xT_yMg_z$ (T = late transition metal) compounds show a strong tendency for a formation of transition metal centered RE_6 trigonal prisms with different condensation patterns and strong RE-T bonding [2].

These $RE_xT_yMg_z$ intermetallics have technical importance for precipitation coarsening in modern light weight alloy systems [3]. The $RE_xT_yMg_z$ compounds with the so far highest rare earth content are the hexagonal ones with $Pr_{23}Ir_7Mg_4$-type structure, space group $P6_3mc$ [4]. They have similar structural features, i.e. a complex network of condensed RE_6T prisms and Mg_4 tetrahedra which fill voids.

The crystal chemical details have been reported in the literature [5 – 8]. The electronic structure, chemical bonding, and physical properties of $Ce_{23}Ru_7Mg_4$ compound have also been reported [9-10]. Unfortunately physical properties at very low temperature (< 2 K) are not available for this compound. Keeping this in mind here we present the physical properties of $Ce_{23}Ru_7Mg_4$ at very low temperature to room temperature. Here we present exploratory results of a study on the novel compound $Ce_{23}Ru_7Mg_4$ which has 68 atoms per unit cell and therefore qualifies as a complex metal alloy.

2. Experimental

A polycrystalline $Ce_{23}Ru_7Mg_4$ sample was synthesized from small cerium ingots (smart elements, > 99.9 %), ruthenium powder (Heraeus, *ca.* 200 mesh, > 99.9 %), and a magnesium rod (Johnson Matthey, ∅ 16 mm, > 99.95 %). Pieces of the cerium ingot were first arc-melted to a small button under purified argon. The cerium button, the ruthenium powder, and pieces of the magnesium rod were then weighed in the 23 : 7 : 4 atomic ratios and arc-welded in a tantalum tube under an argon pressure of about 800 mbar. The ampoule was inductively heated (Hüttinger Elektronik, Freiburg, Type TIG 5/300) first for 2 minutes at about 1300 K, followed by 2 hours at *ca.* 920 K. Finally the tube was quenched to room temperature. The brittle $Ce_{23}Ru_7Mg_4$ sample could easily be separated from the tube. No reaction with the tantalum container was observed. $Ce_{23}Ru_7Mg_4$ crystallizes with the hexagonal $Pr_{23}Ir_7Mg_4$ type structure, space group $P6_3mc$, a = 993.5(3), c = 2243.9(8) pm.

3. Results and discussion

The temperature dependence of inverse magnetic susceptibility of $Ce_{23}Ru_7Mg_4$ between 1.76 and 400 K measured in an applied field of 0.05 T is presented in figure 1. A fit of the inverse magnetic susceptibility in the region 125-400 K according to a modified Curie-Weiss expression $\chi^{-1}(T) = [\chi_0 + C/(T-\theta_P)]^{-1}$ revealed a temperature-independent contribution χ_0 = 0.0004168 emu/Ce-mole, an experimental effective magnetic moment μ_{eff} = 2.24 μ_B/Ce, which is lower than the free ion value of Ce^{+3} $\mu_{eff} = 2.54\mu_B$ and can be attributed to not all cerium atoms being in a trivalent state as the basic building unit of the $Ce_{23}Ru_7Mg_4$ structure is ruthenium centered trigonal prisms formed by cerium atoms which are capped by three further cerium atoms on the rectangular faces. The monomeric building units (trigonal prisms) are condensed via common edges and corners to three-dimensional networks which leave cavities for Mg_4 tetrahedra. In the structure of $Ce_{23}Ru_7Mg_4$ compound, Ce1, Ce2, Ce7, and Ce8 can be considered as trivalent, while Ce3, Ce4, Ce5, Ce6, and Ce9 tend towards intermediate cerium valence. Thus, 30 of the 46 cerium atoms per unit cell are in an intermediate valence state [9-10]. Extrapolation of the $\chi^{-1}(T)$ vs. T data lead to a Weiss constant of $\theta_P = -32.5$ K.

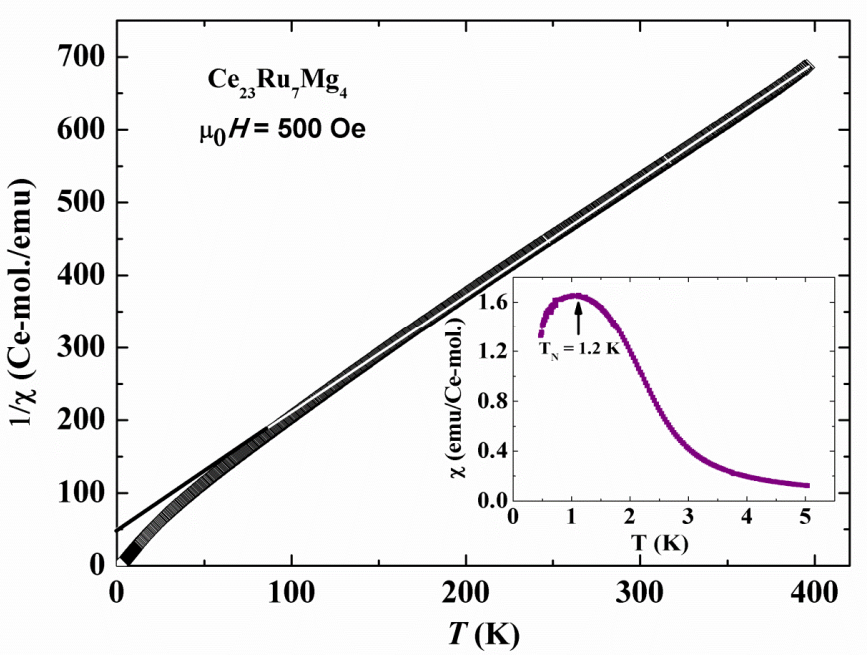

Figure 1. Temperature dependence of the inverse magnetic susceptibility of $Ce_{23}Ru_7Mg_4$ measured in 500 Oe. The line represents the modified Curie-Weiss fit of $\chi^{-1}(T)$. Inset shows the low temperature data of $\chi(T)$, arrow points to the anomaly corresponding to the magnetic phase transition.

The observed negative sign of θ_P can be understood to arise from the development of antiferromagnetic-type correlations between the Ce moments. The attained μ_{eff} value is higher than the obtained value by Linsinger et al. [9]. According to Linsinger et al. μ_{eff} value is 2.01 μ_B/Ce and the θ_P = −13.7 K at applied field 1 T. Below 125 K, the inverse magnetic susceptibility $\chi^{-1}(T)$ considerably deviates from Curie-Weiss behavior, which could be attributed to crystal field splitting of the J = 5/2 ground state of Ce^{+3} and/or the onset of short-range magnetic interactions. With decreasing temperature the magnetic susceptibility exhibits a distinct anomaly due to magnetic ordering which we provisionally attribute to antiferromagnetic type ordering at T_N = 1.2 K. The inset in figure 1 shows the low temperature dependence of $\chi(T)$ with better visible anomaly and the arrow indicating the magnetic phase transition.

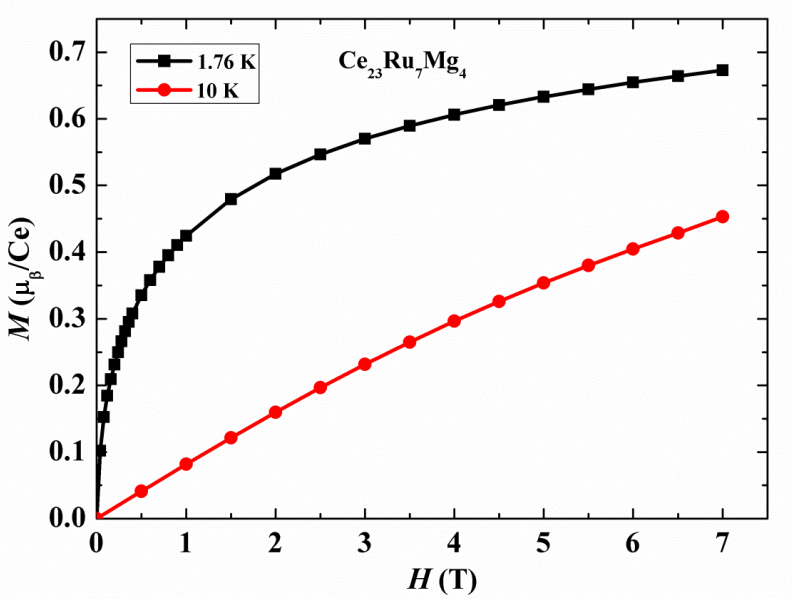

Figure 2. The magnetization for $Ce_{23}Ru_7Mg_4$ at different temperatures.

The magnetization isotherms taken at 1.76 and 10 K are shown in figure 2. The magnetization M increases near linearly with applied magnetic field at temperature T = 10 K, whereas at T = 1.76 K on the other hand a strong curvature in *M* (H) is found. It is noted that the magnetization is especially strongly curved and field dependent in the ≤ 2 T region. The value of magnetic moment measured at 1.76 K in the upper field limit of 7 T amounts to 0.67 μ_B/Ce which is much reduced from the theoretical value for the saturated moment of free Ce^{+3} ion μ_s= 2.14μ_B. It can be accredited to crystal field splitting of the J = 5/2 ground state and owing to the fact that not all Ce atoms are in a stable trivalent state similar to $Ce_{23}Ni_7Mg_4$ [11]. This has also been observed in $Ce_{23}Ru_7Cd_4$ [12]. The magnetic moment value 0.59 μ_B/Ce at 8 T and 2.5 K was obtained by Linsinger et al. [9].

The temperature dependence of the heat capacity $C_P(T)$ of $Ce_{23}Ru_7Mg_4$ in the temperature range 1.94–245K in zero magnetic field is shown in figure 3. The heat capacity measurement of $Ce_{23}Ru_7Mg_4$ shows an upturn starting at about 2 K shown in inset of figure 3. The sharp peak with a maximum at about 2 K in zero field, we ascribe to the transition into a magnetically ordered phase. The appearance of the magnetic phase transition is consistent with measured susceptibility where a pronounced maximum is present near this temperature shown inset in figure 1.

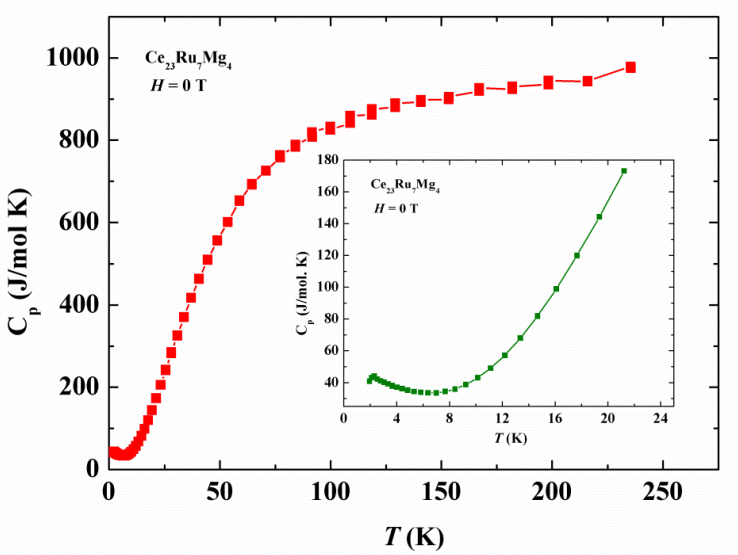

Figure 3. Temperature dependence of the heat capacity of $Ce_{23}Ru_7Mg_4$ up to 245 K in zero magnetic field. Inset: expanded low- temperature part of the heat capacity up to 22 K.

The value of the electronic coefficient of the specific heat γ has been taken as the extrapolation of the linear part of the C_p/T *vs.* T^2 curves at low temperatures indicated by red line displayed in Fig. 4. The upturn in C_p/T *vs.* T^2 observed at low temperatures is related with the magnetic phase transition in low field. The obtained electronic coefficient of specific heat γ value is 127 mJ/Ce-mol·K^2 for $Ce_{23}Ru_7Mg_4$. This value of γ suggests that there may be strong electronic correlations present in $Ce_{23}Ru_7Mg_4$. One origin may be the Kondo effect produced by an on-site hybridization between f and conduction electrons. As a precursor effect to the lower-lying magnetic phase transition however, an enhanced value of γ may also result from short-range correlations immediately above T_N. The value of θ_D obtained from the simplified Debye model is approximately 175 K.

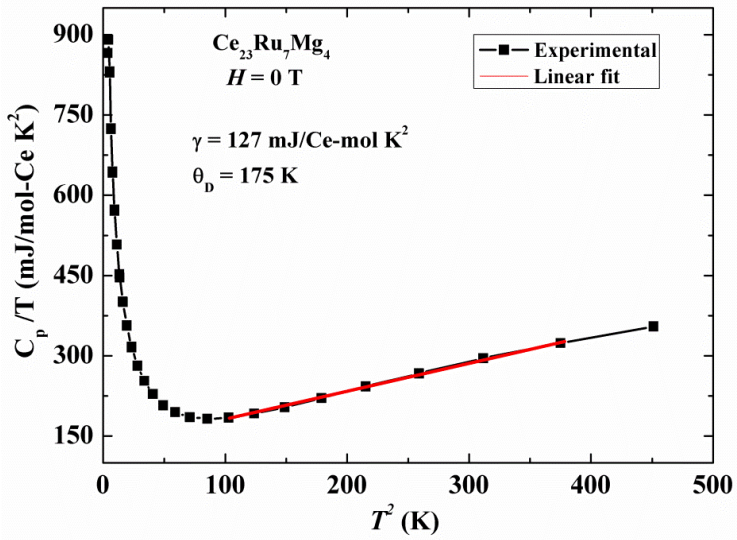

Figure 4. Temperature dependence of the heat capacity displayed as C_P/T *vs* T^2.

The temperature dependence of the heat capacity of $Ce_{23}Ru_7Mg_4$ in zero and 5 T applied magnetic field shown in figure 5. It is shown that with applied magnetic field the peak is flattened and lifted towards higher temperature.

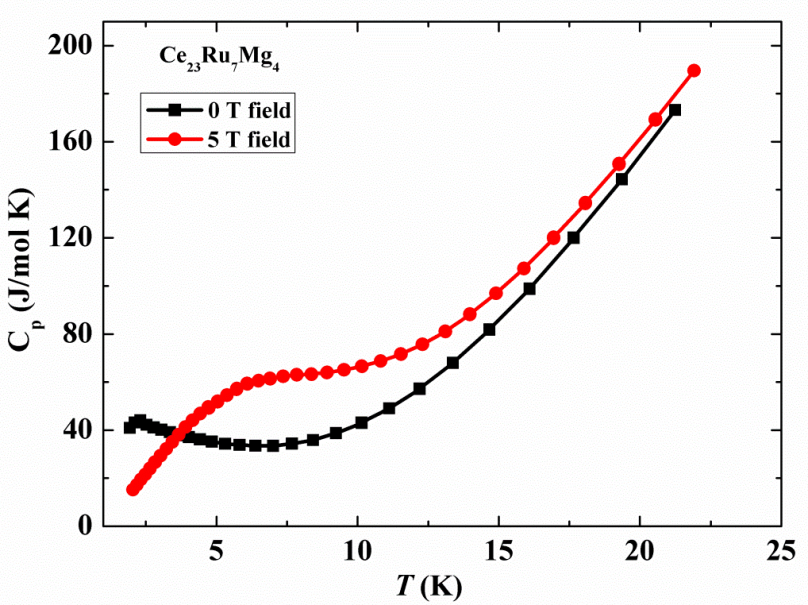

Figure 5. Temperature dependence of the heat capacity in zero and 5 T applied magnetic field.

4. Conclusion

The magnetic susceptibility and heat capacity of $Ce_{23}Ru_7Mg_4$ compound have been studied above room temperature to very low temperature. The magnetic susceptibility exhibits a distinct anomaly at 1.2 K with paramagnetic to antiferromagnetic phase transition. The heat capacity measurement shows a maximum at about 2 K which is almost consistent with the measured susceptibility where strong maximum is present near this temperature. Magnetic susceptibility with paramagnetic to antiferromagnetic phase transition and heat capacity measurements suggests that there may be strong electronic correlations present in $Ce_{23}Ru_7Mg_4$. The heat capacity measurements provide for the electron specific heat coefficient γ = 127 mJ/Ce-mol·K^2 which originates from an appreciable amount of f – electron involvement in the conduction electrons and the resulting strongly hybridized state.

Acknowledgements

JCD acknowledges the NRF (Grant no.85115) for an innovation Postdoctoral Research Fellowship, supervised by AMS. AMS thanks the SA-NRF (78832) and the URC of UJ for financial assistance.

References

[1] Paschen S, Godart C and Grin Y 2011 in Complex metallic alloys: fundamentals and applications, Jean-Marie Dubois; Esther Belin-Ferré (eds.), Weinheim: Wiley-VCH Verlag
[2] Linsinger S, Tuncel S, Hermes W, Eul M, Chevalier B and Pöttgen R 2009 Z. Anorg. Allg. Chem. **635** 282
[3] Kainer K U (Ed.) 2004 Magnesium, Proceedings of the 6th International Conference on Magnesium Alloys and their Applications, Wiley-VCH, Weinheim
[4] Rodewald U Ch, Tuncel S, Chevalier B and Pöttgen R 2008 Z. Anorg. Allg. Chem. **634** 1011
[5] Rodewald U Ch, Chevalier B and Pöttgen R 2007 J. Solid State Chem. **180** 1720
[6] Solokha P, De Negri S, Saccone A, Pavlyuk V, Marciniak B and Tedenac J-C 2007 Acta Crystallogr. **C63** i13
[7] De Negri S, Solokha P, Saccone A and Pavlyuk V 2009 Intermetallics **17** 614
[8] Solokha P, De Negri S, Pavlyuk V and Saccone A 2009 Solid State Sci. 11 801
[9] Linsinger S, Eul M, Hermes W, Hoffmann R-D and Pöttgen R 2009 Z. Naturforsch. **64b** 1345
[10] Matar S F, Chevalier B and Pöttgen R 2012 Intermetallics **31** 88
[11] Tuncel S, Hermes W, Chevalier B, Rodewald U Ch and Pöttgen R 2008 Z. Anorg. Allg. Chem. **634** 2140
[12] Tappe F, Hermes W, Eul M and Pöttgen R 2009 Intermetallics **17** 1035