Physical properties of the layered structure compound $Ce_3Os_4Al_{12}$

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Abstract. In this work, we report on the structural and physical properties of polycrystalline $Ce_3Os_4Al_{12}$ synthesized by the argon arc-melting technique. The Rietveld refinement of powder X-ray diffraction patterns confirm that $Ce_3Os_4Al_{12}$ crystallizes in the hexagonal $Gd_3Ru_4Al_{12}$-structure type with space group $P6_3/mmc$. The temperature dependent dc-magnetic susceptibility and specific heat data reveals that the compound undergoes a ferromagnetic type of ordering below 3 K. The study may contribute towards a better understanding of the physics in distorted Kagomé structure compounds, since in a frustrated lattice system such as this, there are strict constraints imposed upon the occurrence of long-range magnetic order and the magnetic order parameter.

1. Introduction

$R_3T_4X_{12}$ type of compounds are of particular interest among intermetallics because the crystal structure contains layers as well as triangular and distorted Kagomé lattice features [1, 2, 3]. The arrangement of the atoms carrying magnetic moments at the vertices of the structure and the competition between ferro- and antiferromagnetic interactions can lead to the appearance of magnetic frustration phenomena. Several studies have been done on Ru-based compounds in this series of aluminides. In these Ru-based compounds, a ferromagnetic behavior is observed in the light rare-earth based compounds (Pr and Nd) [2, 3, 4] while an antiferromagnetic behavior is observed in the heavy rare-earth ones (Gd, Tb, Dy and Yb) [5, 6, 7]. For instance, in $Gd_3Ru_4Al_{12}$, geometrical frustration together with the formation of ferromagnetic trimers due to the long-range RKKY interaction is observed at low temperatures [5]. Moreover, a skyrmion lattice with large topological Hall effect has been experimentally observed in the same material [8]. Skyrmions have good potential for information carriers in spintronic devices and frustration is a route towards enhanced skyrmion stability even in systems with a ferromagnetic ground state [9]. In $Pr_3Ru_4Al_{12}$, a magnetic moment instability in the presence of crystal electric fields is observed [2]. Despite the number of studies carried out in the $R_3Ru_4Al_{12}$ series, no physical and magnetic properties have been reported yet on Os-based compounds (except on $Gd_3Os_4Al_{12}$) synthesized for the first time by Niermann [10]. This work is the first report on physical properties of $Ce_3Os_4Al_{12}$.

2. Synthesis and experimental details

A polycrystalline sample was synthesized by arc-melting stoichiometric amounts of high-purity (99.99 mass % purity or better) elements (Ce, Os and Al) under argon atmosphere in an Edmund Buhler arc-melting furnace. After melting, the sample was annealed in a resistance furnace at 900^{o}C for two weeks and finally water quenched. Dc-magnetic susceptibility, isothermal magnetization and specific heat measurements were performed using a commercial Dynacool physical properties measurement system from Quantum Design, USA. The measurements were carried out in the temperature range between 1.8 K to 300 K and fields up to a maximum value of 9 T.

3. Results and Discussion

The powder x-ray diffraction spectrum of this sample (see Fig. 1) was successfully refined on the basis of the hexagonal $Gd_3Ru_4Al_{12}$ structure type with P63/mmc space group. The structure was refined to R_{wp} = 6.84 %, R_p = 4.49 % and R_{exp} = 0.98. The obtained lattice parameters are $a = 0.889(1)$ nm and $c = 0.953(1)$ nm. These values are in good agreement with an earlier report [10]. The refined atomic positions are reported in table 1.

The crystal structure may be described as a layered structure. The Ce atoms occupy only one site in the Ce_3Al_4 layer. The Ru atoms share two sites and the Al atoms occupy two different sites in the Os_4Al_8 puckered layer (see Fig. 2). The Ce atoms are arranged as a distorted Kagomé net with different sizes of triangles leading to two slightly different nearest-neighbour Ce-Ce distances.

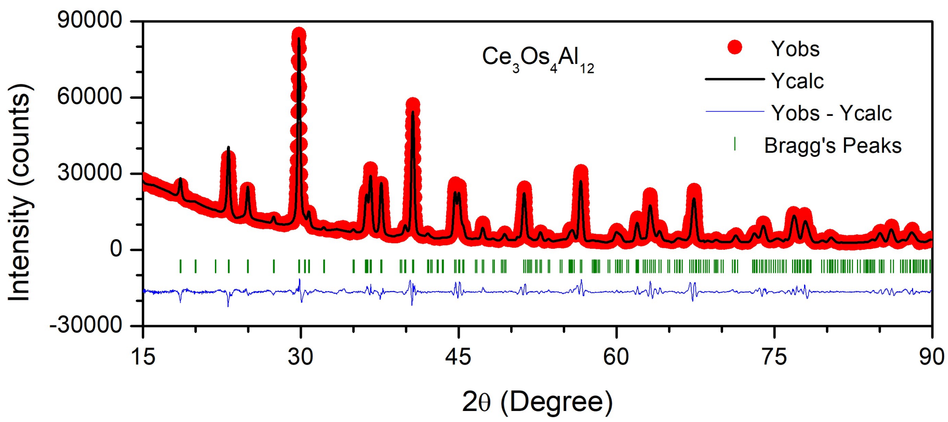

Figure 1. (a) Layered representation of the crystal structure of $Ce_3Os_4Al_{12}$ with Ce (Orange spheres), Os (blue spheres) and Al (green). (b) The Ce_3Al_4 layer showing the distorted Kagomé nets.

The main panel of Fig. 3 represents the dc-magnetic susceptibility $\chi(T)$ of $Ce_3Os_4Al_{12}$ measured in a magnetic field of 0.1 T. The data are obtained in a field-cooled protocol (cooling of the sample from 300 K to 2 K). $\chi(T)$ exhibits a modified Curie-Weiss behavior described by equation (1) from 300 K down to 50 K:

$$\chi(T) = \chi_0 + C/(T - \theta_P), \quad (1)$$

where χ_0 is the temperature independent susceptibility, C is the Curie-Weiss constant, and θ_P is the paramagnetic Weiss temperature. From the least-squares fit of equation (1) to the data, we obtained an effective magnetic moment (μ_{eff}) of 0.54 μ_B/Ce ion which is less than one quarter

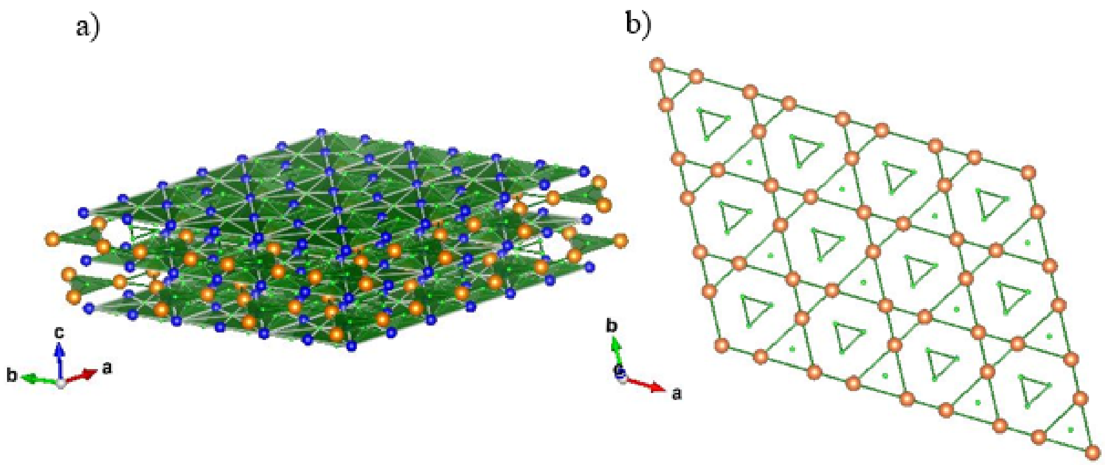

Figure 2. (a) Layered representation of the crystal structure of $Ce_3Os_4Al_{12}$ with Ce (Orange spheres), Os (blue spheres) and Al (green). (b) The Ce_3Al_4 layer showing the distorted Kagomé nets.

Table 1. Crystallographic details of $Ce_3Os_4Al_{12}$.

Atom	Wyckoff	x	y	z	Occupancy
Ce	6h	0.19174	0.38348	0.25000	0.19211
Os_1	6g	0.50000	0.00000	0.00000	0.30492
Os_2	2a	0.00000	0.00000	0.00000	0.11893
Os_3	6h	0.00000	0.00000	0.25000	0.11893
Al_1	12k	0.16523	0.33046	0.57419	0.42748
Al_2	6h	0.53125	0.12953	0.25000	0.02533
Al_3	4f	0.33333	0.66667	0.02753	0.19764
Al_4	2b	0.00000	0.00000	0.25000	0.05803

of the theoretical value of a free trivalent Ce ion (2.54 μ_B) in $Ce_3Os_4Al_{12}$. This suggests either an itinerant character or a strong crystal field effect of the 4f-electrons in $Ce_3Os_4Al_{12}$. The paramagnetic Weiss temperature is found to be $\theta_P = +5.3$ K with the positive sign indicating the dominance of ferromagnetic interactions in the high temperature region. The kink observed around the transition temperature T_c=3 K (see inset (a) of Fig. 3) is a sign of a short-range order-like transition. Isothermal magnetization at temperatures between 2 K and 20 K is presented in the inset (b) of Fig. 3. Broad curvatures are observed below 6 K. The saturation magnetization at 2 K and in 9 T is only about 0.06 μ_B/Ce ion which is less than 5% of the full saturation value compared to the free ion saturation value 2.16 μ_B/Ce. The quasi-linear behavior above 6 K indicates a paramagnetic state.

The main panel of Fig. 4 represents the specific heat of $Ce_3Os_4Al_{12}$ and $La_3Os_4Al_{12}$ as function of temperature. The high temperature region resembles the behavior of a normal metal. Inset (a) of Fig 4 represents the low-temperature region. The blue symbols represent the magnetic 4f contribution to the specific heat obtained by subtracting the specific heat of $La_3Os_4Al_{12}$ from that of $Ce_3Os_4Al_{12}$. The kink observed around the transition temperature T_c=3 K is a sign of a short-range order-like transition. Inset (b) shows the 4f contribution to the entropy per Ce as a function of temperature. The magnetic contribution released at T_c is about 0.6 J/mole$_{Ce}$.K^2 which is about 10% of the value Rln2 expected for a doublet ground

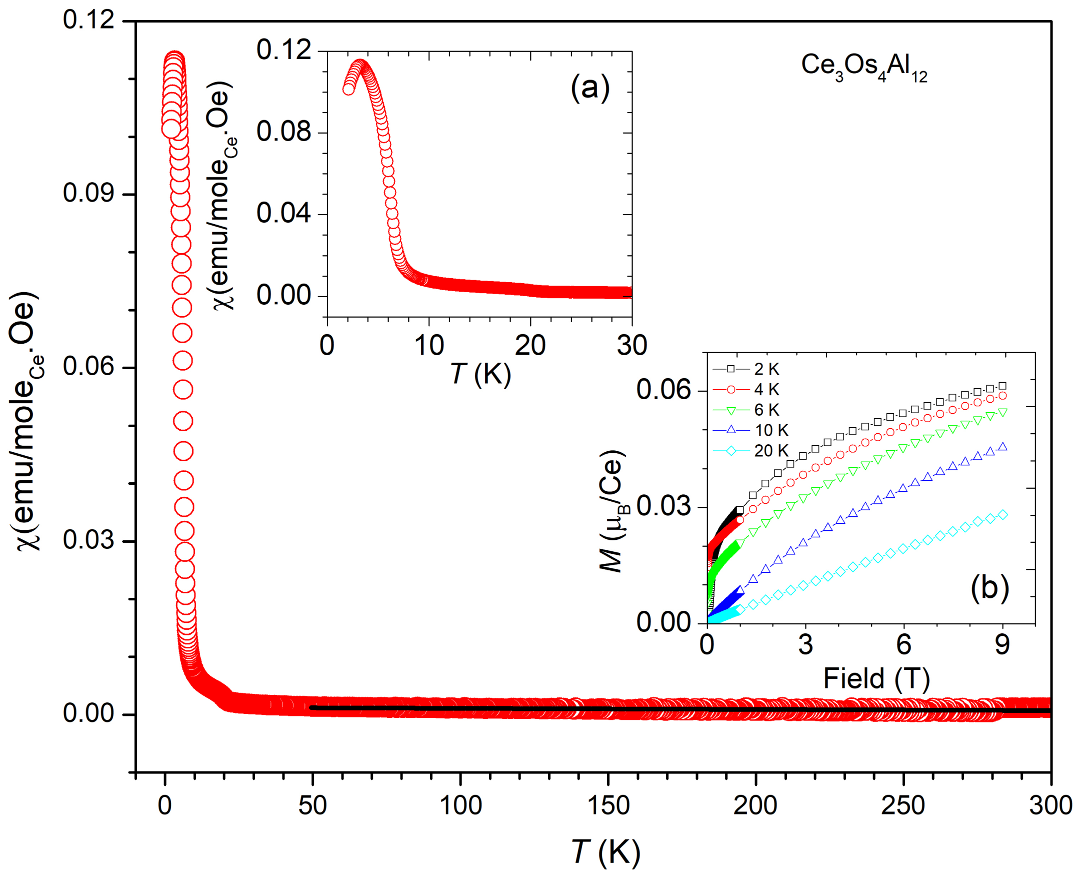

Figure 3. Main panel: magnetic susceptibility of $Ce_3Os_4Al_{12}$ measured in a constant dc-magnetic field of 0.1 T. The black line represents the least-squares fit of the modified Curie-Weiss relation (see equation 1). Inset (a) highlights the low-temperature region. Inset (b) represents the isothermal magnetization at temperatures between 2 K and 20 K.

state of the crystal field split multiplet of trivalent Ce. Inset (c) of Fig 4 represents the specific heat $C_{4f}(T)/T$ vs T^2. $C_{4f}(T)/T$ at $T \to 0$ reaches 0.4 $J/mol_{Ce}.K^2$ which is enhanced by a factor of 100 above that of an ordinary metal [11]. This points to a large residual 4f-electron entropy in the low-temperature limit which is likely caused by strong electron correlations in the Ce compound.

4. Conclusion

$Ce_3Os_4Al_{12}$ is a new example of a layered distorted Kagomé structure with possible effects of the geometric frustration. The $\chi(T)$ and $C_p(T)$ data confirm the presence of weak magnetic order. Further magnetic studies are needed to describe in detail the nature of the phase transition observed in $Ce_3Os_4Al_{12}$.

4.1. Acknowledgments

RFD thanks OWSD and SIDA for fellowships towards her PhD studies. B. Sahu thanks Global Excellence and Stature (UJ-GES) fellowship, University of Johannesburg. AMS thanks the URC/FRC of UJ and the SA-NRF (93549) for financial support.

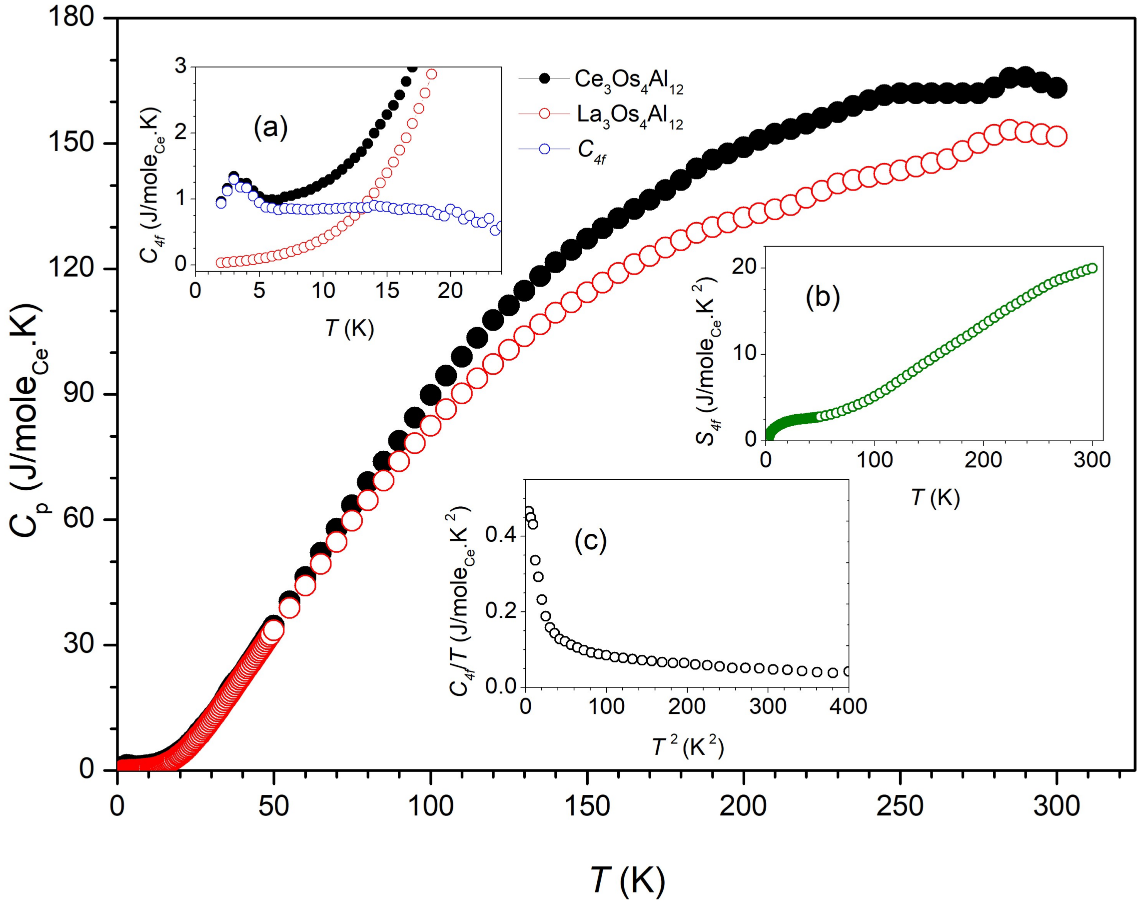

Figure 4. Main panel: Specific heat of $Ce_3Os_4Al_{12}$ and $La_3Os_4Al_{12}$ against temperature. Inset (a) represents the low-temperature region. The blue symbols represent the 4f-electron contribution to the specific heat of $Ce_3Os_4Al_{12}$ obtained by subtracting the specific heat of $La_3Os_4Al_{12}$ from that of $Ce_3Os_4Al_{12}$. Inset (b) shows the 4f contribution to the entropy per Ce as a function of temperature. Inset (c) illustrates $C_{4f}(T)/T$ vs T^2.

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