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# Magnetic and Thermodynamic Properties of $Ce_4RuAl$

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The results of magnetic susceptibility and heat capacity measurements are reported for the $Ce_4RuAl$ compound above room temperature to low temperature range (400 K to 0.34 K) and in the magnetic field up to 7 T. The magnetic susceptibility $\chi(T)$ exhibits a distinct anomaly at 0.95 K which most probably suggests a paramagnetic to antiferromagnetic phase transition. The magnetic susceptibility obeys the Curie–Weiss law in the region 100–400 K and revealed an effective magnetic moment $\mu_{\rm eff} = 2.18\ \mu_{\rm B}$/Ce which is less than the value for free $Ce^{3+}$ ($\mu_{\rm eff} = 2.54\ \mu_{\rm B}$). The paramagnetic Weiss temperature indicates net antiferromagnetic correlations. In the specific heat a peak at 1.3 K supports the bulk nature of the phase transition observed in $\chi(T)$. The Sommerfield coefficient is moderately enhanced in the paramagnetic phase, and suggests f–c correlations among the electrons prior to magnetic ordering. The obtained Sommerfield coefficient $\gamma$ behavior is consistent with the Anderson model-based theoretical predictions.

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## 1. Introduction

Rare-earth elements are characterized by an incompletely filled $4f$ shell, which is small compared to typical interatomic distances in metallic compounds and usually carry a stable and well defined magnetic moment even in metallic compounds. A large number of rare-earth compounds exhibit unusual low-temperature properties, which are ascribed to interactions of the localized $4f$ moments with their environment. The crystal electric field (CEF) at the rare-earth ion site splits the free-ion ground-state multiplet. The temperature-dependent occupation probability of the CEF levels is reflected in many physical properties [1]. Intermetallic cerium compounds have widely been investigated in the last 40 years with respect to their intriguing physical properties [2]. This is due to the peculiar valence behavior, i.e. trivalent cerium has a $[Xe]^4f^1$ configuration and exhibits paramagnetism (often accompanied by magnetic ordering), while tetravalent cerium, $[Xe]^4f^0$, is diamagnetic. Various examples are known where the cerium valence can be influenced by temperature [3], by pressure [4], or upon hydrogenation [5].

As part of our program to explore new compounds to broaden our understanding of the physics of the strongly correlated electron class of materials, results of a variety of physical properties have been provided in this work to probe the magnetic and electronic behavior of the $Ce_4RuAl$ compound. To date, exploratory studies on $Ce_4RuAl$ have been reported at a conference [6] and by Tappe et al. [7]. In the present paper, we report the physical properties of the Ce–Ru–Al system, namely $Ce_4RuAl$. We have measured the susceptibility and magnetization of $Ce_4RuAl$ from 400 K to 0.5 K.

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## 2. Experimental

The sample of $Ce_4RuAl$ was prepared by arc melting the stoichiometric amounts of the constituent elements on a water-cooled copper hearth in argon atmosphere. All the metals had a purity of 99.99%. All the materials were melted at least four times and turned over after every melting to ensure homogeneous mixing. Powder X-ray diffraction was obtained using Cu $K_\alpha$ radiation. Magnetization and heat capacity measurements were carried out using standard physical and magnetic measurement systems from Quantum Design (San Diego).

## 3. Result and discussion

Figure 1 shows the temperature dependence of magnetic susceptibility and inverse magnetic susceptibility $\chi^{-1}(T)$ between 1.76 to 400 K for $Ce_4RuAl$ measured in an applied field of 0.05 T. A fit of the inverse magnetic susceptibility in the region 100-400 K according to a modified Curie–Weiss expression $\chi^{-1}(T) = [\chi_0 + C/(T-\theta_P)]^{-1}$ revealed a temperature-independent contribution $\chi_0 = 0.0003668$ emu/(Ce mol), a magnetic moment $\mu_{\rm eff} = 2.18\ \mu_{\rm B}$/Ce, and the Weiss temperature $\theta_P = -81.33$ K.

This $\mu_{\rm eff}$ value is higher than the obtained value by Tappe et al. [7]. According to Tappe et al. $\mu_{\rm eff}$ value is 1.74 $\mu_{\rm B}$/Ce and the $\theta_P = -34.1$ K at applied field $B =$ 1 T. At low temperatures, the inverse magnetic susceptibility $\chi^{-1}(T)$ considerably deviates from Curie–Weiss behaviour, which could be attributed to the crystalline-electric-field (CEF) effect. More experiments such as high-resolution angle-resolved photoemission studies and inelastic neutron scattering measurements are required to estimate the CEF parameters. The observed negative sign of $\theta_P$ can be understood to arise from the development of antiferromagnetic-type correlations between the Ce moments.

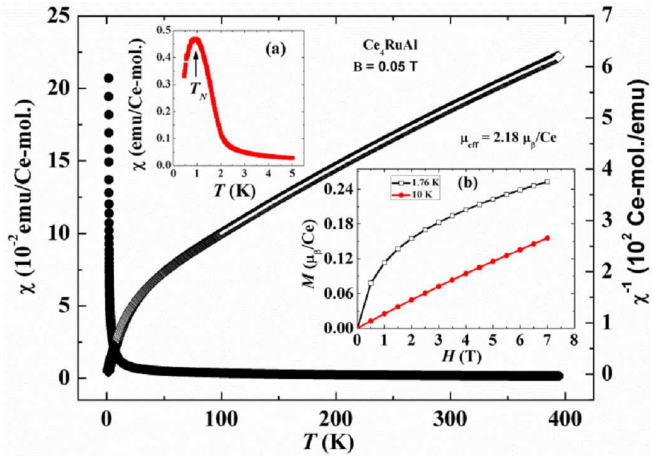


Fig. 1. Temperature dependence of the magnetic susceptibility and inverse susceptibility of $Ce_4RuAl$ measured in 0.05 T. The line represents the modified Curie-Weiss fit of $\chi^{-1}(T)$. Inset (a) shows the low temperature data of $\chi(T)$, arrow points to the anomaly corresponding to the magnetic phase transition. Inset (b) shows the magnetization for $Ce_4RuAl$ at different temperatures.

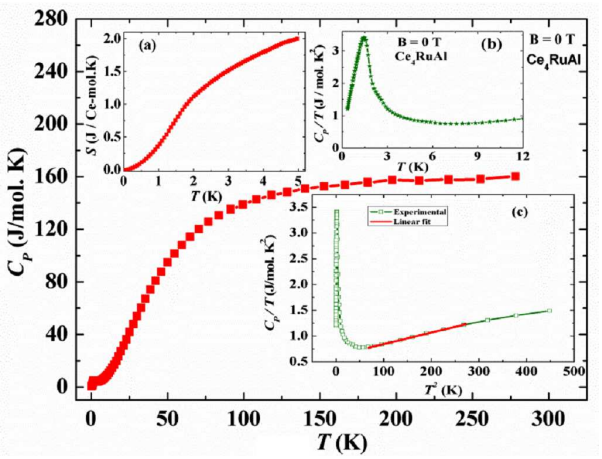


Fig. 2. Temperature dependence of the heat capacity of $Ce_4RuAl$ up to 300 K in zero magnetic field. Inset (a): The corresponding entropy as a function of temperature. Inset (b): Temperature dependence of the heat capacity displayed as $C_P/T$ Inset (c): a low temperature part of the heat capacity.

With decreasing temperature the magnetic susceptibility exhibits a distinct anomaly due to magnetic ordering at $T_N = 0.95$ K. The inset (a) in Fig. 1 shows the low temperature dependence of $\chi(T)$ with better visible anomaly and the arrow indicating the magnetic phase transition.

The magnetic field dependence of magnetization at different temperatures for $Ce_4RuAl$ is presented in inset (b) of Fig. 1. The magnetization $M$ increases 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 $\leq 2$ T region. The value of magnetic moment measured at 1.76 K in a field of 7 T amounts to 0.25 $\mu_B$/Ce which is much lower than the theoretical value for the saturated moment of free $Ce^{+3}$ ion $\mu_s = 2.14$ $\mu_B$. It is probable that magnetocrystaline anisotropy plays an important role here. The obtained magnetic moment value is lower than the obtained value by Tappe et al. [7].

Figure 2 shows the temperature dependence of the heat capacity $C_P(T)$ of $Ce_4RuAl$ in the temperature range 0.5–300 K in zero magnetic field. The value of the electronic coefficient of the specific heat $\gamma$ 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 exposed in inset (c) of Fig. 2. The upturn in $C_P/T$ vs. $T^2$ observed at low temperatures is presumably related with the magnetic phase transition in low field[see inset (b) of Fig. 2]. The obtained electronic coefficient of specific heat $\gamma$ value is 158 mJ/(Ce mol $K^2$) for $Ce_4RuAl$.

This value of $\gamma$ suggests that there may be strong electronic correlations present in $Ce_4RuAl$. 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 $\gamma$ may also result from short-range correlations immediately above $T_N$. The value of $\theta_D$ obtained from the simplified Debye model is approximately 174 K. Inset (c) of Fig. 2 shows the low-temperature part (0.35 K to 12 K) of the heat capacity ($C_P/T$ vs. $T$) of $Ce_4RuAl$ in zero field.

We ascribe the sharp peak with a maximum at about 1.3 K in zero field, to the transition into a magnetically ordered phase. The appearance of the magnetic phase transition is consistent with measured susceptibility where strong maximum is present near this temperature shown in inset (a) in Fig. 1 where the magnetic susceptibility has a rapid decrease at 0.95 K. The magnetic contribution to the specific heat and the corresponding magnetic entropy are related to the energy levels of the magnetic ions. In the absence of a nonmagnetic homologue with which to assess the lattice contribution, we show in inset (a) of Fig. 2 the total entropy of this system, which should be viewed as an upper limit of its $4f$ magnetic entropy. At $T_N$ the obtained value of $S$ reaches about 14% for the case of a doublet ground state. The CEF effect of $Ce^{3+}$ in cubic crystal symmetry is expected to split into one doublet and one quartet. Thus, our results support the view that even if all three site symmetries occupied by Ce in this structure, see [7], should participate in the magnetic ordering then the $Ce^{3+}$ ions would still have to be in a strongly hybridized state to be concomitant to such a tiny fraction of the full available magnetic entropy of the $4f$ spin system. Such a hybridized $Ce^{3+}$ state in $Ce_4RuAl$ was in fact alluded to in the observed anomalous contraction of $Ce_4RuAl$ lattice parameter values in the $R_4RuAl$ series [7].

Figure 3 shows the low temperature part of $C_P/T$ vs. $T$ for $Ce_4RuAl$ in various applied magnetic fields. Due to the anomalous behavior at low temperatures the

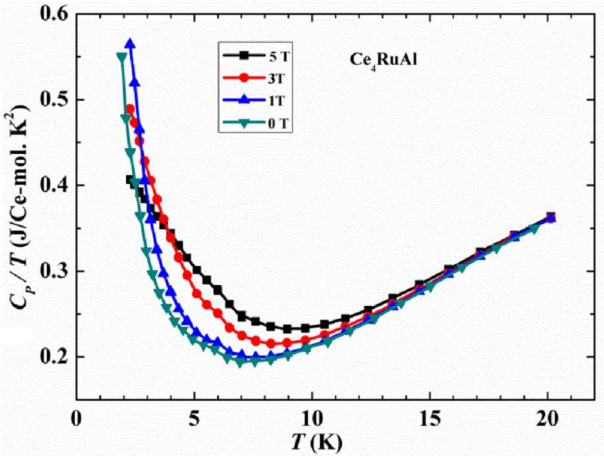


Fig. 3. Effect of magnetic field on the specific heat of $Ce_4RuAl$.

$\gamma$ coefficients value depend strongly on the temperature range used for the extrapolation and on the magnetic field. It evolves from the 158 to 180 mJ/(Ce mol $K^2$) for (H) increasing from 0 to 5 T. The obtained $\gamma$ behavior is consistent with the Anderson model-based theoretical predictions [8].

## 4. Conclusions

Magnetic susceptibility with paramagnetic to antiferromagnetic phase transition and heat capacity measurements suggest that there may be strong electronic correlations present in $Ce_4RuAl$. The heat capacity measurements provide $\gamma = 158$ mJ/(Ce mol $K^2$ for the electron specific heat coefficient showing that there is an enhancement of the effective mass. The enhanced value of $\gamma$ originates from an appreciable amount of $f$-electron involvement in the conduction electrons and the resulting strongly hybridized state. The obtained $\gamma$ behavior for different applied fields is consistent with the Anderson model-based theoretical predictions.

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