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# Strongly Correlated Electron Behaviour in $\text{CeT}_2\text{Al}_8$ ( $T = \text{Fe, Co}$ )

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We report on studies of physical properties of the two compounds  $\text{CeFe}_2\text{Al}_8$  and  $\text{CeCo}_2\text{Al}_8$  in which we have found varying degrees of electronic correlational phenomena. No magnetic ordering was detected down to 0.4 K in either of the two compounds. At elevated temperatures an incoherent Kondo interaction between the Ce  $4f$ -electron and the conduction electrons is prevalent in both compounds.  $\text{CeCo}_2\text{Al}_8$  exhibits a stable  $4f$ -electron magnetic moment, but in  $\text{CeFe}_2\text{Al}_8$  an intermediate-valent state prevails near room temperature that eventually transforms into a Fermi-liquid ground state. The low-temperature specific heat of  $\text{CeCo}_2\text{Al}_8$  shows typical strongly correlated electron behaviour and a  $-\log T$  upturn in its electronic specific heat below about 10 K.

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## 1. Introduction

Intermetallic compounds comprising magnetic  $f$ - and  $d$ -electron elements in which hybridization with conduction electrons results in enhanced densities of states close to the Fermi energy beget a wealth of physical phenomena. As part of our program to explore new compounds and crystal structures to broaden our understanding of the physics of the strongly correlated electron class of materials, we report in this work results of a variety of physical properties on the  $\text{CeT}_2\text{Al}_8$  pair of compounds in which  $T = \text{Fe}$  and  $\text{Co}$ .

Exploratory magnetic properties of  $X = \text{Al}$  and  $\text{Ga}$  derivatives were reported [1, 2] after formation of the nominal  $\text{CeT}_2\text{X}_8$  stoichiometry type was established. The findings on  $\text{CeFe}_2\text{Al}_8$  that lead Koterlin et al. [2] to conclude that the magnetism in this compound is governed by intermediate valence arising from strong  $c$ - $f$  hybridization prompted Mössbauer [3] and neutron diffraction [4] studies to investigate aspects of the ground state. Electrical resistivity and thermoelectric studies [5] lead to characterizing  $\text{CeCo}_2\text{Al}_8$  as a Kondo lattice. In the present work, we extend investigations into the pair of compounds  $\text{CeFe}_2\text{Al}_8$  and  $\text{CeCo}_2\text{Al}_8$  by means of specific heat, magnetization, and electrical resistivity studies. We argue that the ground state in both compounds is governed by the  $c$ - $f$  hybridization, but with contrasting outcomes. In  $\text{CeFe}_2\text{Al}_8$  a metallic Fermi-liquid ground state is achieved with negligible enhancement in the electronic density of states at low temperatures due to very strong hybridization. The situation is more subtle in  $\text{CeCo}_2\text{Al}_8$  on the other hand, and here a heavy Fermi-liquid and proximity to magnetic order are found to be key issues in determining this compound's ground state.

## 2. Experiments and results

Polycrystalline specimens of  $\text{CeFe}_2\text{Al}_8$  and  $\text{CeCo}_2\text{Al}_8$  together with their nonmagnetic La counterparts were

prepared by direct melting of stoichiometric quantities of the elements (purity in weight%) Ce (99.99), Fe and Co (99.99+), and Al (99.999) in an argon-arc furnace with *in situ* argon purification. Annealing was performed for all 4 compounds at 900 °C for 21 days. Physical properties were studied on a commercial Physical Property Measurement System [6] equipped with a  $^3\text{He}$  insert. For magnetic properties, a Magnetic Property Measurement System [6] was used for applied magnetic fields up to 7 T. Sample temperatures down to 460 mK were achieved for magnetic measurements by means of an iQuantum  $^3\text{He}$  insert [7].

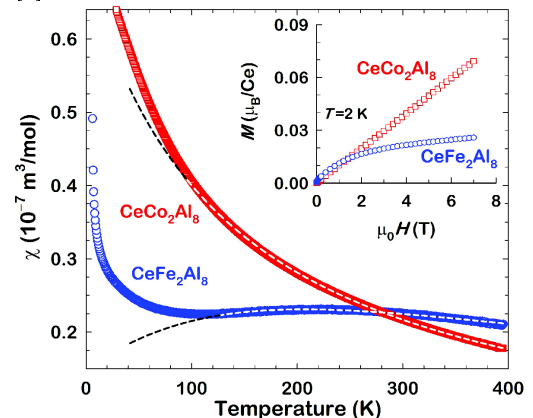


Fig. 1. Magnetic susceptibility  $\chi(T)$  of  $\text{CeFe}_2\text{Al}_8$  (blue) and  $\text{CeCo}_2\text{Al}_8$  (red) measured in a constant field of 0.05 T. The  $\chi(T)$  scale is expanded to clarify the least-squares fits of an intermediate valence model ( $\text{CeFe}_2\text{Al}_8$ ) and the Curie-Weiss law ( $\text{CeCo}_2\text{Al}_8$ ). Inset: magnetization of  $\text{CeFe}_2\text{Al}_8$  and  $\text{CeCo}_2\text{Al}_8$  at 2 K.

The samples were all proven to be single-phase by powder X-ray diffraction and the calculated lattice parameters agreed well with literature values. In the case of the novel member in this series,  $\text{LaCo}_2\text{Al}_8$ , we have determined  $a(\text{Å}) = 12.98(1)$ ,  $b = 14.32(1)$ ,  $c = 4.17(1)$ , and hence the orthorhombic unit-cell volume  $V = 775.52(1) \text{ Å}^3$  in the space group  $Pb3m$  (no. 55) which is common to this series. Further details of crystal-

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lographic data resulting from this work will be published elsewhere.

The higher-temperature magnetic susceptibilities  $\chi(T)$  of the two compounds  $\text{CeFe}_2\text{Al}_8$  and  $\text{CeCo}_2\text{Al}_8$  measured in a small field of 0.05 T are shown in Fig. 1 (main part). In  $\text{CeFe}_2\text{Al}_8$  a steady loss of magnetic moment and turnaround in  $\chi(T)$  first results in a broad maximum followed by a minimum in  $\chi(T)$  near 120 K. It is noted that the higher-temperature susceptibility data of  $\text{CeFe}_2\text{Al}_8$  presented by Kolenda et al. [4] as well as those of Tamura et al. [3] were conducted in a much higher field of 1 T and failed to reveal this subtle variation found in  $\chi(T)$ . We interpret this magnetic feature of  $\text{CeFe}_2\text{Al}_8$  along a model for intermediate-valence proposed by Sales and Wohleben [8]. A system with two available valence states described by the Boltzmann statistics with  $\text{Ce}_n^{3+}$ ;  $J_n = 5/2$ ;  $\mu_{\text{eff},n} = 2.54 \mu_B$  and  $\text{Ce}_{n-1}^{2+}$ ;  $J_{n-1} = 0$ ;  $\mu_{\text{eff},n-1} = 0$ , means that the fractional occupation of state  $n$  reduces to

$$\nu(T) = (2J_n + 1) / [(2J_n + 1) + \exp(-E/(T + T_{\text{sf}}))]. \quad (1)$$

Here  $E = E_n - E_{n-1}$  is the energy separating the two valence states.  $T_{\text{sf}}$  is a characteristic temperature scale which separates the higher temperature region where thermal excitations determine the relative occupation between the two states and hence the net magnetic response, from the lower temperature region where quantum-mechanical fluctuations describe the degeneracy. The magnetic susceptibility of the system becomes

$$\chi(T) = N(\mu_{\text{eff},n})^2 \nu(T) / 3(T + T_{\text{sf}}). \quad (2)$$

The fit depicted on the  $\chi(T)$  data of  $\text{CeFe}_2\text{Al}_8$  in Fig. 1 was obtained with  $T_{\text{sf}} = 270(2)$  K, which is close to the observed local maximum in  $\chi(T)$ . The illustrated fit is commensurate with a slowly increasing population of the magnetic  $J = 5/2$  state of Ce as  $\text{CeFe}_2\text{Al}_8$  is cooled down, but at room temperature the population is still only about  $\nu(300 \text{ K}) \approx 0.45$ . The susceptibility of  $\text{CeCo}_2\text{Al}_8$  on the other hand follows stable-moment Curie-Weiss behaviour.

The value  $\mu_{\text{eff}} = 2.45(2) \mu_B$  and a Weiss temperature of  $\theta_P = -136(1)$  K yielded the fit for  $\text{CeCo}_2\text{Al}_8$  illustrated in Fig. 1. This suggests a net antiferromagnetic exchange between magnetic moments in this compound. The magnetic situation in  $\text{CeFe}_2\text{Al}_8$  involving strongly hybridized Ce  $4f$ -electrons appears to be a common trend among Ce-Fe type compounds such as  $\text{CeFe}_2$  [9],  $\text{CeFe}_4\text{Sb}_{12}$  [10], and  $\text{CeFe}_4\text{P}_{12}$  [11]. A special outcome of this type of hybridization is the Kondo insulating state that occurs in  $\text{CeFe}_2\text{Al}_{10}$  [12] for example. Temperature-dependent Mössbauer studies [3] established that in  $\text{CeFe}_2\text{Al}_8$  neither Ce nor Fe bears a magnetic moment. This result is consistent with our findings of a strongly hybridized Ce ion which achieves an effective loss of magnetic moment. The inset in Fig. 1 illustrates magnetization of the two Ce compounds at 2 K. In 7 T,  $\text{CeCo}_2\text{Al}_8$  yields  $\approx 3$  times greater magnetic response compared to the Fe compound.

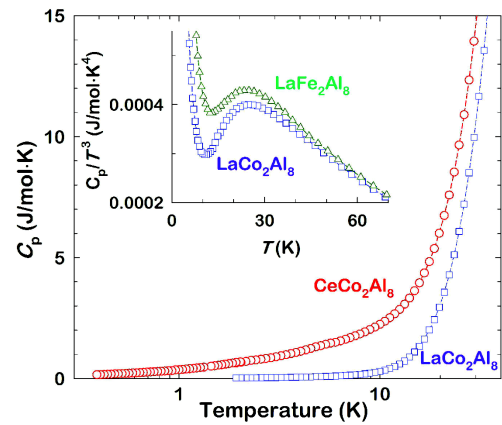


Fig. 2. Semi-log plot of the specific heat of the two Co compounds  $\text{LaCo}_2\text{Al}_8$  (blue) and  $\text{CeCo}_2\text{Al}_8$  (red) to emphasize the difference at low temperatures. Inset: specific heat of the two nonmagnetic compounds  $\text{LaFe}_2\text{Al}_8$  and  $\text{LaCo}_2\text{Al}_8$  shown in the form  $C_p/T^3$  vs.  $T$  to expose the presence of optical phonon excitation modes in these two compounds.

Figure 2 (main panel) shows a considerable excess of specific heat  $C_p$  in  $\text{CeCo}_2\text{Al}_8$  over that of its nonmagnetic counterpart  $\text{LaCo}_2\text{Al}_8$ . Using  $C_p(T)$  of the La compound to quantify the lattice and nonmagnetic contribution is commonly used to compute the magnetic  $4f$ -electron derived contribution of  $C_p(T)$  in the Ce compound. In the present case however, we show in the inset of Fig. 2a  $C_p(T)/T^3$  plot against temperature which suggests irregular phononic behaviour in the two La compounds. This form of the specific heat is seen to peak near  $T_{\text{max}} \approx 25$  K, and thus indicates a sizeable presence of optical phonons in the excitation spectra of  $\text{LaFe}_2\text{Al}_8$  and  $\text{LaCo}_2\text{Al}_8$ . It is noted that this feature was not found in either of the two magnetic compounds  $\text{CeFe}_2\text{Al}_8$  and  $\text{CeCo}_2\text{Al}_8$ .

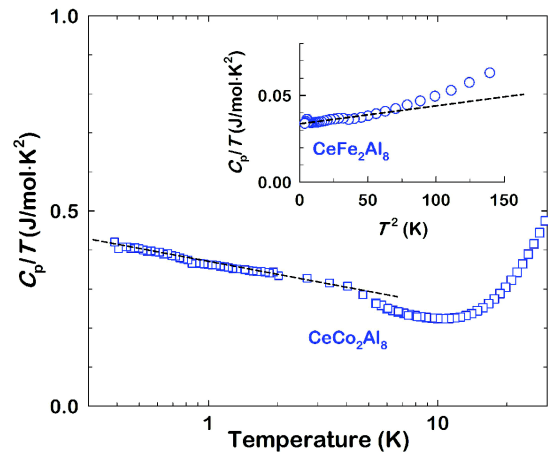


Fig. 3. Low-temperature specific heat of  $\text{CeCo}_2\text{Al}_8$  in the form  $C_p(T)/T$ . The dashed line simulates a  $-\log T$  dependence below 3 K. Inset:  $C_p(T)/T$  of  $\text{CeFe}_2\text{Al}_8$ .

Figure 3 (main panel) illustrates low-temperature behaviour of the specific heat  $C_p(T)/T$  of  $\text{CeCo}_2\text{Al}_8$ . Cooling below 10 K produces an upturn in  $C_p(T)/T$  and in fact below  $T \approx 3$  K  $C_p(T)/T$  traces a  $-\log T$  dependence over more than a decade in temperature. This behaviour of the specific heat in strongly correlated electron systems has become the hallmark of non-Fermi-liquid behaviour originating from a magnetic quantum critical point. Measurements at lower temperatures are needed to investigate the possibility of lower-lying magnetic order. The low-temperature specific heat of  $\text{CeFe}_2\text{Al}_8$  (Fig. 3, inset) on the other hand is metallic, somewhat enhanced, and returns a Sommerfeld coefficient amounting to  $\gamma \approx 34(1)$  J/(mol K<sup>2</sup>).

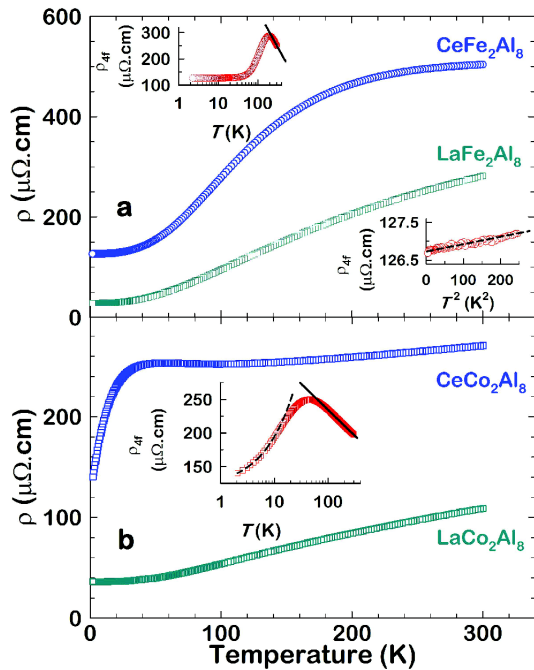


Fig. 4. Electrical resistivity of (a)  $\text{LaFe}_2\text{Al}_8$  and  $\text{CeFe}_2\text{Al}_8$ , and (b)  $\text{LaCo}_2\text{Al}_8$  and  $\text{CeCo}_2\text{Al}_8$ . Insets show the magnetic part of the resistivities of  $\text{CeFe}_2\text{Al}_8$  and  $\text{CeCo}_2\text{Al}_8$ .

We turn in the final instance to results of electrical resistivity  $\rho(T)$  in Fig. 4. The results are in fair comparison with the available literature [2, 5]. A  $\rho_{4f}(T) \sim -\log T$  dependence of the  $4f$ -electron derived  $\rho(T)$  is found at higher temperatures (see solid lines in insets), a form of scattering that originates in incoherent Kondo-type scattering of charge carriers from local moments. Closer inspection reveals an important difference between the two Ce compounds: in  $\text{CeFe}_2\text{Al}_8$ ,  $\rho_{4f}(T)$  achieves a maximum at  $\approx 200$  K with an overall behaviour attributed to a strongly hybridized, intermediate-valent state of Ce. At low temperatures  $\rho(T)$  of  $\text{CeFe}_2\text{Al}_8$  follows a Fermi-liquid-like  $\rho_{4f}(T) \sim T^2$  behaviour, see

Fig. 4a, dashed line in inset. In  $\text{CeCo}_2\text{Al}_8$ , on the other hand,  $\rho_{4f}(T)$  achieves a maximum at the much lower temperature of 45 K. Considering its total resistivity, the decrease found in  $\rho_{4f}(T)$  has its roots in a Kondo-lattice effect of phase-translation coherence among  $4f$ -electron local moments. The low-temperature resistivity in this case rather follows a non-Fermi-liquid power law,  $\rho_{4f}(T) \sim T^n$  with  $n = 0.76(1)$ , see dashed line in Fig. 4b, inset.

The two compounds  $\text{CeT}_2\text{Al}_8$  ( $T = \text{Fe}, \text{Co}$ ) display interesting variations in their correlational behaviour. The sensitive nature of the  $4f^1$  state is attributed primarily to variations in the electronic environment of Ce. Further low-temperature measurements are in progress.

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