Transport properties of strongly correlated electron systems Ce$\boldsymbol{T}_2$Al$_8$(T= Fe,Co)

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Abstract. We present specific heat, thermopower, and thermal conductivity, on the two novel rare earth intermetallic compounds $CeFe_2Al_8$ and $CeCo_2Al_8$ and its nonmagnetic isostructural compounds $LaFe_2Al_8$ and $LaCo_2Al_8$ respectively. These compounds are crystallizes in orthorhombic crystal structure having a space group *Pbam* (no.55). In the unit cell representation Ce atom occupies only one lattice site having Ce-Ce interatomic distance is 4.043(1)Å and 4.044(1)Å for $CeFe_2Al_8$ and $CeCo_2Al_8$ respectively. A reduced magnetic moment is observed in $CeFe_2Al_8$ around 100K in susceptibility measurement which echoed an intermediate valence state in Ce^{3+} ion. On the other hand for $CeCo_2Al_8$ the local moment state is depicted through an effective moment close to free Ce^{3+} ion value. No long-range magnetic ordering is found in either of the two compounds down to 1.9 K. Below 2 K, the electronic specific heat of $CeCo_2Al_8$ reaches γ=0.167J/mol-K^2, and exhibits a $-lnT$ divergence towards T$\rightarrow$0 is indicative of strong correlation effects in this compound, whereas at lower temperature $CeFe_2Al_8$ shows metallic type of behaviour. In studies of the thermoelectric power, a maximum is reached at T=140 K (S=24μV/K) and T=30 K (S=23μV/K) for $CeFe_2Al_8$ and $CeCo_2Al_8$ compounds respectively. The thermal conductivity $\kappa(T)$ of these polycrystalline samples varies as $\kappa(T) \sim T^2$ within the temperature range of 1.9 K-100 K is attributed to electron-phonon scattering in these systems.

1. Introduction

Strongly correlated electon systems with unstable 4f-electronic states have been very attractive for last decades. A specific feature of this class of compounds having high value of certain physical properties, like thermopower (S), electrical resistivity (ρ), magnetic susceptibility (χ) and electronic coefficient of specific heat (γ), which is 10 - 10^3 times higher than typical metal. Among the rare earth elements Ce and Yb based compounds are interesting because the nature of the 4f-electronic state near the Fermi level which is responsible for physical properties such as intermediate valence state (IVS), heavy fermion nature, Kondo type of interaction,and superconductivity[1, 2]. The recent finding of interesting physical properties of filled skutterudite and clathrates compounds are also promising candidates for novel thermoelectric materials[3, 4, 5]. $CeFe_2Al_8$, $CeCo_2Al_8$ and its non-magntic La compounds were crystallizes in orthorhombic crystal structure having a space group *Pbam*[6]. Magnetic and thermoelectric properties of these compounds were measured by Kotlein et al.[7, 8, 9], indicating a Kondo lattice system with unstable 4f- electronic state. According to the Mössbauer studies [10, 11] Fe site in this system does not have a magnetic moment and hence magnetic properties orginate due to rare earth(RE^{3+}) ions. Here we present the ground state physical properties of the two title compounds and its non-magnetic lanthanum compounds in continuation of our investigations into competing magnetic interactions in strongly correlated electron systems.

2. Experiments

Polycrystalline samples $CeFe_2Al_8$, $CeCo_2Al_8$ and its isostructural, nonmagnetic counterpart $LaFe_2Al_8$, $LaCo_2Al_8$ were prepared by arc melting the constituent elements under a highly purified argon atmosphere with additional Ti-getting inside the furnace. The weight losses after melting were less than 0.5wt% for all compounds. All compounds were wrapped with a Ta-foil, sealed in an evacuated quatrz tube annealed at 900^0C for 3 weeks and subsequently quenched in water. The quality of all 4 annealed compounds were checked by means of X-ray powder diffraction on Philips Pan Analytical XPert Pro instrument with Cu-Kα_1 radiation. Rietveld refinements program (GSAS) were used to calculate the lattice parameters of these annealed compounds. All refined lattice parameters are listed in table1. Microprobe analysis was performed to verify the chemical compositions of $CeFe_2Al_8$, $CeCo_2Al_8$ and $LaFe_2Al_8$, $LaCo_2Al_8$ compounds. Analysis was done using 20μm diameter beam on carbon coated polished surface using CAMECA SX-100 electron microprobe. No unreacted elements were detected in microprobe technique and proved the samples are in single phase. Temperature variations of electrical resistivity and specific heat in the range between 1.9 K-300 K were studied using Quantum Design PPMS device in zero magnetic field equipped with ^{3}He low-temperature facilities. Magnetic susceptibility and magnetization were studied in the temperature range between 1.9 K-400 K and in applied fields up to 7Telsa using a MPMS-XL superconducting quantum interference device magnetometer.

Table 1. Crystal data, refined lattice parameters, coefficient of thermal conductivity(α, β and γ) and figure of merit (ZT) of Ce and La compounds.

Compounds	$CeFe_2Al_8$	$CeCo_2Al_8$	$LaFe_2Al_8$	$LaCo_2Al_8$
Formula weight(g/mol)	467.658(3)	473.834(7)	466.447(8)	472.624(2)
Lattice parameters(Å)	a=12.490(6)	a=12.480(6)	a=13.103(1)	a=12.980(1)
	b=14.400(8)	b=14.390(9)	b= 14.346(1)	b= 14.321(1)
	c=4.043(2)	c=4.041(2)	c= 4.175(2)	c= 4.107(4)
Volume(Å^3), Z	727.157(7), 4	725.285(8), 4	784.798(5), 4	775.518(3), 4
Calculated density(g/cm^3)	4.272(2)	4.312(1)	3.705(1)	3.975(3)
Bond length(Å)	d_{Ce-Ce}=4.043(1)	d_{Ce-Ce}=4.044(1)	d_{La-la}= 4.175(1)	d_{La-La}= 4.172(1)
α (m/W)	1.63(2)	6.86(2)	2.76(1)	4.43(2)
β (m-K^3/W)	2.358(5)$\times10^{-5}$	5.027(1)$\times10^{-5}$	2.731(1)$\times10-5$	2.225(2)$\times10^{-5}$
δ (W/m-K^3)	3.850(2)$\times10^{-4}$	3.622(2)$\times10^{-4}$	4.360(1)$\times10^{-4}$	4.270(2)$\times10^{-4}$
ZT(at 300K)	0.221(1)$\times10^{-2}$	0.570(1)$\times10^{-4}$	0.368(3)$\times10^{-2}$	0.351(4)$\times10^{-4}$

3. Results

3.1. Specific heat

Fig.2 (main panels) shows the specific heat $C_P(T)$/T vs. T of $CeFe_2Al_8$, $CeCo_2Al_8$ and its non-magnetic La compounds in lower temperature region. Inset fig.2(a) and (b) shows electronic contribution of specific heat after substracting from La compounds. The Sommerfeld coefficient

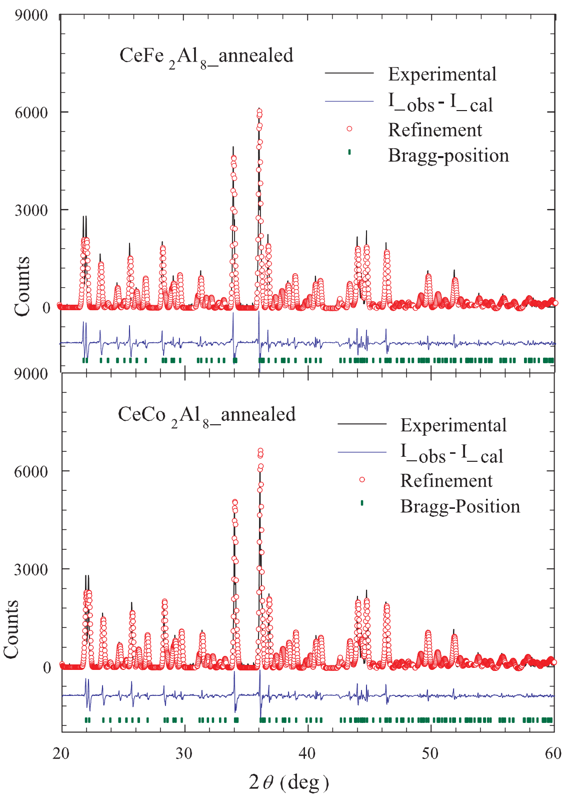

Figure 1. Powder X-ray diffractrogram recorded for annealed $CeFe_2Al_8$ and $CeCo_2Al_8$ compounds at room temperature.Circle(red)through experimental line is the Rietveld refinement fit (using GSAS). The lower curve(blue) represents the difference between the observed and calculated results and the Bragg-positions were marked by vertical bar(green). Calculated lattice parameters are listed in table1.

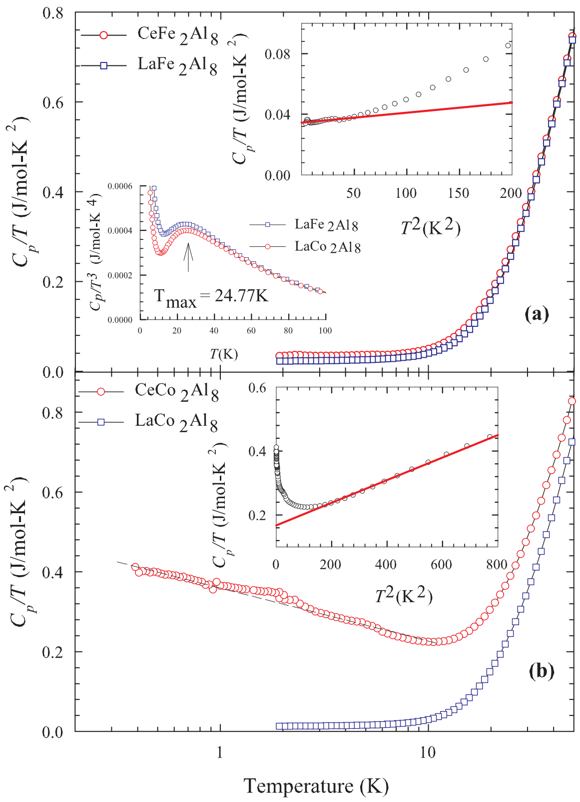

Figure 2. (main panels)Semi-log plot of the specific heat of Ce and La compounds at lower temperatures regions. The dashed line in $CeCo_2Al_8$ indicates $-lnT$ dependence in specific heat as $T\ \rightarrow 0$. The lower Inset fig.2(a) shows $C_P(T)/T^3$ vs.T plot. The upper inset fig.2(a) and (b) are illustrates a plot of $C_P(T)/T$ vs.T^2 to facililate calculation of the Sommerfeld coeffieicent, as explained in the text.

γ of all compounds were calculated according to the relation

$$C(T)/T = \gamma + \beta T^2, \gamma = \frac{\pi}{2}\frac{N_A k_B^2}{E_F}, \beta = \frac{12\pi^4}{5} N_A k_B \frac{1}{\theta_D^3} \tag{1}$$

where γ is electronic contribution related to density of states, β is lattice contribution of specific heat, N_A is Avogadro number,k_B is Boltzmann constant, E_F is Fermi energy and θ_D is Debye temperature.

Important difference were exposed between two Ce compounds when cooling down below 10 K produces an upturn in $C_P(T)$/T and in fact below 3 K $C_P(T)/T$ traces a $-lnT$ divergence over more than a decade in temperature. At 2 K electronic specific heat of these compound reaches γ= 0.167 J/mol.K^2 and β=0.353 mJ/mol-K^4. The divergence behaviour of the specific heat in $CeCo_2Al_8$ system has become the hallmark of non-Fermi liquid behaviour originating from a magnetic quantum critical point. On the other hand $CeFe_2Al_8$ follows normal Fermi liquid type of behaviour at lower temperature with γ= 34.4 mJ/mol-K^2 and β= 0.065 mJ/mol-K^4. Lower inset fig.2(a) a $C_P(T)/T^3$ plot against Temperature wich suggest irregular phononic behaviour in the two La compounds. This form of the specific heat is seen to peak near T_{max}= 24.77 K, and thus indicating a sizeable presence of optical phonons in the excitation spectra of $LaFe_2Al_8$ and $LaCo_2Al_8$ compounds. It is noted that this feature was not found in either of the two magnetic compounds $CeFe_2Al_8$ and $CeCo_2Al_8$.

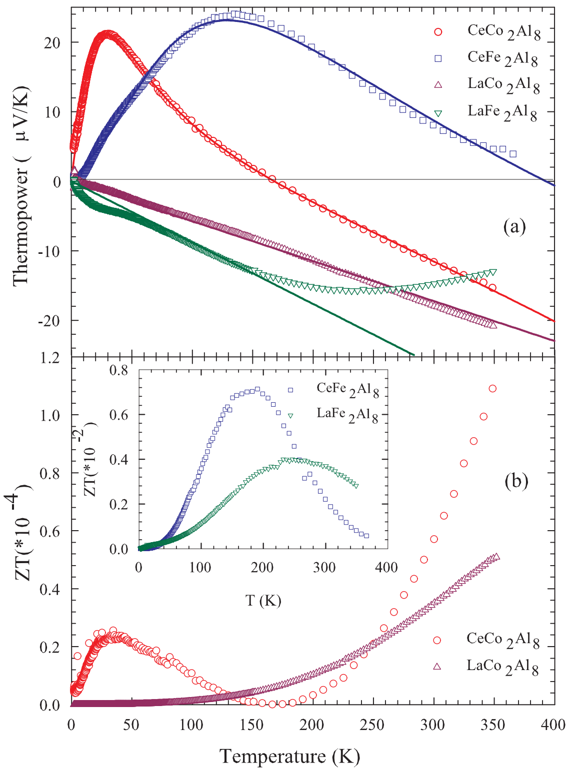

Figure 3. (a) Temperature variations of thermopower $S(T)$ of Ce and La compounds. Solid line is the fit according to the Eq.(2). (b) temperature dependence of dimensionless figure of merit (ZT) of $CeCo_2Al_8$ and $LaCo_2Al_8$, and (inset) $CeFe_2Al_8$, and $LaFe_2Al_8$ compounds.

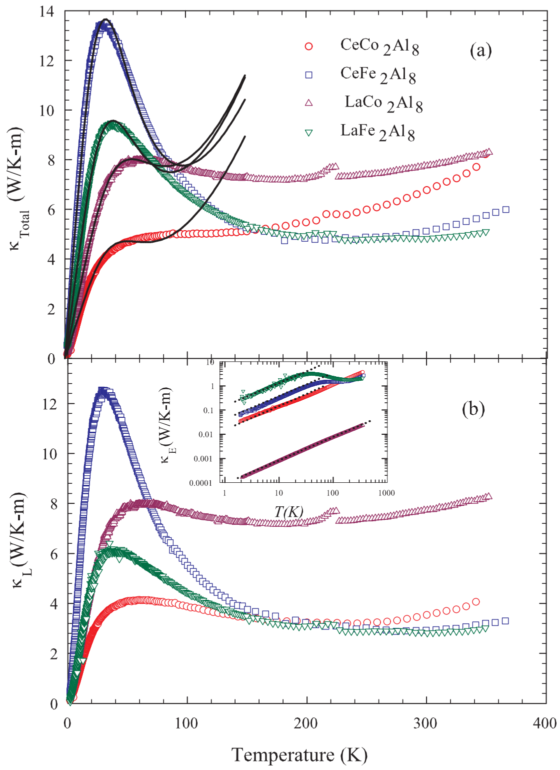

Figure 4. (a) Temperature dependence total thermal conductivity (κ_{Total}). Solid lines is the fit according to the Eq.(5). (b) κ_E(inset,log-log scale) and κ_L were calculated from the Wiederman-Franz law as expalined in the text. The dotted line emphasize the linear behaviour of $\kappa_E(T)$.

3.2. Thermopower

In fig.3(a) the temperature dependence of thermoelectricpower(TEP), $S(T)$, of the two Ce compounds $CeFe_2Al_8$ and $CeCo_2Al_8$ and its iso-structural La compounds $LaFe_2Al_8$ and $LaCo_2Al_8$ are shown together with calculated cuves in the temperature ranage between 1.9 K-400 K. One can see a large maximum of $S(T)$ at 140 K and 30 K for $CeFe_2Al_8$ and $CeCo_2Al_8$ compounds respectively. It is well established that in a Kondo systems TEP is mainly due to competition between crystal electric field effects (CEF) and Kondo effets[12, 13]. We have carried out an analysis of the measured thermopower basing on the model assuming scattering of electrons from the wide s-d conduction band into a strongly correlated narrow f-band approximated by a

Lorentzian shape[14, 15]. TEP is then expressed by the formula

$$S(T) = \frac{2}{3}\frac{k_B\pi^2}{|e|}\sum_{i=1}^{2}\frac{E_{fi}T}{(\pi^2/3)T^2 + E_{fi}^2 + W_{fi}^2} + aT \tag{2}$$

where E_f and W_f are the position and width of the f-band in Kelvin. Eq.2 has been satisfactory used to described the two Ce compounds in wide temperature range. The calculated fitting parametrs are E_{f1}= -2.246 K, W_{f1}= 145.632 K, E_{f2}= 220.30 K, W_{f2}= 7.287 K and a= -0.049μV/K^2 for $CeFe_2Al_8$, and E_{f1}= 182.94 K, W_{f1}= 1308.41 K, E_{f2}= 56.27 K, W_{f2}= 8.19 K and a= -0.104μV/K^2 for $CeCo_2Al_8$. It result from these parameters that eq.2 emerging two Lorentzian peaks within the region of the Fermi level, were saperatued by a quasi energy gap Δ= $|E_{f1}|$+$|E_{f2}|$= 0.019eV and Δ= $|E_{f1}|$+$|E_{f2}|$= 0.020eV for $CeFe_2Al_8$ and $CeCo_2Al_8$ respectively. One of the peaks lies nearly at the Fermi level, whereas the second one is relatively far away from the E_F. The linnear term aT is added in the above equation to fit the thermopower over entire temperature region, where parameter 'a'in general be responsible for several effects but is mainly due to the nonmagnetic Mott-type scattering[16, 17], which is determined by the Fermi energy. Whereas the thermopower of both La compounds are large negative values and linear behabiour $S(T)$= -αT is usually releated to free-electron model as shown in fig.3(a).

3.3. Thermal conductivity

Figure 4(a) shows the total thermal conductivity of $CeCo_2Al_8$,$CeFe_2Al_8$ and $LaCo_2Al_8$,$LaFe_2Al_8$ compounds measured as a function of temperture. We extarct the the electronic contribution κ_E to the total heat conductivity by means of the Wiedemann-Franz relation, for which the thermal conductivity is, in a highly degenerate electron gas, releated to σ, the electrical conductivity by the relation:

$$L_0 = \frac{\kappa}{\sigma T}, L_0 = \left(\frac{\pi k_B}{e\sqrt{3}}\right)^2 = 2.45\times 10^{-8} W\Omega K^{-2} \tag{3}$$

The electrical conductivity $\sigma(T)$ and the thermal conductivity $\kappa(T)$ used in this expression, as well as a thermopower $S(T)$, were measured simultaneously with the same set of contacts to the samples. The total thermal conductivity κ_{Total} of simple metal consist of electronic and lattice contributions can be expressed as

$$\kappa_{Total} = \kappa_E + \kappa_L, \kappa_E = \kappa_{E,0} + \kappa_{E,L} \tag{4}$$

where$(E, 0)$ and (E, L) as contribution due to the interaction of the conduction electrons with static imperfections and thermally excited phonons respectively. On the hand $\kappa_L \sim 1/T$ at high temperature(phonon-phonon-umklapp procress) and at lower temperature $\kappa_L \sim T^2$ due to interaction of phonons with conduction electrons. At low temperature regions between 1.9 K-100 K thermal conductivity of Ce and La compounds follows a T^2 dependence and we model it according to the relation[18]:

$$\kappa_{Total} = \kappa_E + \kappa_L = \frac{1}{\alpha/T + \beta T^2} + \delta T^2 \tag{5}$$

A least square fit of the Eq.5 to the total thermal conductivity data of Ce and La compounds are shown in fig.4(a). The coefficient of thermal conductivity are listed in table 1. A plateau in $\kappa_L(T)$ or a very weak temperature dependence of κ_L are acheived in $LaCo_2Al_8$ and $LaFe_2Al_8$ compounds upward about 100 K. We consider this plateau region is due to the effects of rattling atoms, in La compounds of which were implied in the analysis of the specific heat measurements in section 3.1. Local anharmonic vibration from the rattling atoms are known to be effective resonant scatterers for heat carring acoustic phonons. A dip or plateau like feature found in (lattice) thermal conductivity of filled or partially filled skutterudites and clathrates compounds[19].These materials are being studied extensively as they are considered ameanable to the phonon-glass approch to designing materials for high value of thermoelectric merit[20, 21]. The overall thermal conductivity suggested that phonons contribution were dominated in transport properties, i,e $\kappa_{Total} \cong \kappa_L$ is these compounds. In contrast to the phononic part, the electronic thermal conductivity $\kappa_E(T)$ of Ce and La compounds shows a metallic type of behaviour and practically $\kappa_E(T)$ is linear in T are shown in inset fig.4(b). Finally, we present the dimensionless thermoelectric figure of merit, ZT, as a function of temperature in fig.3(b). ZT values for Fe based compounds ($CeFe_2Al_8$ and $LaFe_2Al_8$) is 100 times larger than Co based compounds ($CeCo_2Al_8$ and $LaCo_2Al_8$) at room temperature are listed in table 1.

3.4. Conclusion

The Ce compounds ($CeFe_2Al_8$ and $CeCo_2Al_8$) and its isostructural La compounds ($LaFe_2Al_8$ and $LaCo_2Al_8$) display interesting variations in their correlation behavior. Physical properties of these compounds are sensitive to the nature of $4f^1$ state and the variations in electronic environment of Ce atom. In these systems depending on the elements $T=$ Fe,Co a variation from Fermi liquid to non-Fermi liquid behabiour are observed. TEP of these compounds in the whole temperature range were studied and satisfactory described assuming two Lorentzian peaks located below and above the fermi level in the density of state. Futher lower temperature analysis are still under progress.

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