La substitution induced linear temperature dependence of electrical resistivity and Kondo behavior in the alloys, Ce$_{2-x}$La$_x$CoSi$_3$

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The results of electrical resistivity ($\rho$), heat-capacity (C) and magnetic susceptibility ($\chi$) measurements (above 1.5 K) for the alloys of the type, Ce$_{2-x}$La$_x$CoSi$_3$, are reported. We find that the S-shaped temperature dependence of $\rho$ for the mixed-valent $x=0.0$ alloy is not a single-ion property; the most interesting observation is that, for an intermediate concentration, ($x=0.25$), linear temperature dependence of $\rho$ below 30 K is noted, an observation of relevance to the current trends in the topic of non-Fermi-liquid behavior. Other observations are: (i) Ce exhibits single-ionic heavy-fermion behavior with moderately enhanced electronic contribution to C; and (ii) the strength of the Kondo interaction, as measured by the Curie-Weiss parameter gets reduced for larger substitutions ($x>0.5$) of La for Ce.

KEY WORDS: D. heavy fermions; D. Kondo effects; D. Electronic transport; D. heat capacity
The ternary rare-earth (R) compounds of the type, R$_2$TX$_3$ (T= transition metals, X = Si, Ga), derived from AlB$_2$-type hexagonal structure have attracted considerable attention in the recent past [1-14]. Perhaps this class of rare-earth intermetallics will be one of the most extensively studied ones next to ThCr$_2$Si$_2$-type structure. Among these, the compound, Ce$_2$CoSi$_3$, is of special interest, as the crystallographic analysis reveals ordering of cobalt atoms within the CoSi$_3$ hexagonal layer and also Ce appears to be in a mixed-valent state [8]. In this article, we present the results of electrical resistivity ($\rho$), heat-capacity ($C$) and magnetic susceptibility ($\chi$) measurements for the alloys, Ce$_{2-x}$La$_x$CoSi$_3$, in order to probe how the lattice expansion caused by La substitution for Ce modifies the properties of this compound, particularly to see whether any of these alloys exhibit non-Fermi liquid (NFL) behavior, considering current interest in this direction of research in condensed matter physics.

The samples, Ce$_{2-x}$La$_x$CoSi$_3$ (x = 0.0, 0.25, 0.5, 1.0, 1.5 and 2.0), have been prepared by melting together stoichiometric amounts of constituent elements in an arc furnace in an atmosphere of argon. The samples were annealed at 750$^\circ$C for one week and then characterized by x-ray diffraction and the diffraction lines could be indexed on the basis of an AlB$_2$-derived structure. It appears [8] that the unit cell along the basal plane is twice that of AlB$_2$-structure, and the lattice constant s derived for this solid solution (Fig. 1) reveal an expansion of the unit-cell with La substitution for Ce, as expected. The $\rho$ measurements (1.5-300 K) were performed by a conventional four-probe method employing a silver-paint for making electrical contacts of the leads with the samples. The C measurements (2-50 K) were performed by a semi-adiabatic heat-pulse method. The $\chi$ data (2 - 300 K) were taken employing a superconducting quantum interference device in a magnetic field (H) of 2 kOe.

The results of $\rho$ measurements are shown in Fig. 2. Not much significance could be attached to the absolute values of $\rho$ considering that the samples are very brittle and porous and hence the data are normalised to respective 300 K values. The $\rho$ of the parent Ce compound (x= 0.0) decreases with temperature (T) with a significant, but continuous fall with T below about 100 K approaching a constant value at low temperatures. The shape of resistivity versus T plot (usually called S-shaped) observed for this composition is typical of mixed-valent Ce compounds like CeSn$_3$ (Ref. 15). There are qualitative changes in the shape of $\rho$ versus T plots with the substitution of La for Ce. It is interesting to note that small substitutions (x= 0.25) of La for Ce transforms low temperature (below 30 K) $\rho$ behavior to a linear T dependence (NFL behavior), retaining positive T coefficient of $\rho$; there is a slight deviation from the low temperature linear behavior around 30 K as the temperature is increased, followed by another linear region in the range 30 - 100 K. For the next higher content of La (x= 0.5), there is a feeble minimum in $\rho$ around 50 K (seen only if the low temperature data is plotted in an expanded scale), indicative of the single-ion Kondo effect, though there is a small drop of $\rho$ below 10 K the origin of which is not clear. For a further addition of La, a well-defined Kondo minimum in the plot could clearly be seen. Thus, the S-shaped behavior of the plot of $\rho$ versus T for x= 0.0 is not a single-ion property and the data demonstrate Kondo lattice to single-ion Kondo transformation by La substitution.

The results of C measurements are shown in Fig. 3. It is to be noted that there is no evidence for the existence of a prominent $\lambda$-type anomaly for any of the alloys in the entire temperature range of investigation. This establishes that the parent Ce compound is non-magnetic and the possible reduction of the Kondo interaction caused by La substitution is not sufficient to drive Ce towards magnetic ordering. For x= 0.0, there is however an extremely small peak around 6 K, which was observed even in an earlier work [8] and it is not clear whether it is intrinsic; it is possible that this peak arises from small traces (estimated to be around 1%, below the detection limit of x-ray diffraction) of trivalent Ce oxide. The plot of C/T versus T (Fig. 4) shows an upturn at low temperatures in all cases reaching values above 100 mJ/Ce mol K$^2$ at about 2 K, presumably arising from the electronic contribution thereby indicating heavy-fermion character of Ce in this chemical environment. It is not clear whether this feature signals NFL nature of the low temperature state of all these alloys. The value of C/T extrapolated from the linear regime (12 - 20 K) is also large falling in the range 60 - 80 mJ/Ce mol K$^2$. We subtracted the lattice contribution to C from the knowledge of C values of La analogue; we observe that the 4f contribution to C thus obtained divided by T is independent of T in the range 4 - 20 K, thereby suggesting that there is no influence of possible high temperature Schottky anomalies in
Ce-based Kondo lattices, La substitution tends to drive Kondo effects. To probe whether this NFL behavior persists in such compounds, we extend the measurements to low temperatures (below 1 K). The plot of inverse χ versus T is found to be non-linear in the entire temperature range of investigation, presumably due to large temperature independent contribution (Pauli susceptibility). Assuming that this contribution is the same as the χ value of La$_2$CoSi$_3$ at 300 K (4 × 10$^{-4}$ emu/mol), we subtract this contribution for each composition. The values thus obtained (after normalising to Ce concentration) are shown in Fig. 5 in the form of the plot of inverse χ versus T. We are now able to clearly see a linear region in the range 100 - 300 K. The effective moment obtained from this range turns out to be very close to 2.5 µ$_B$, typical of trivalent Ce ions for all the compositions and the Curie-Weiss parameter, θ$_p$ (± 10 K) is found to be - 240, -230, -250, -140, and -140 K for x = 0.0, 0.25, 0.5, 1.0 and 1.5 respectively. The trivalency of Ce and large negative θ$_p$ value for x= 0.0, combined with a large low temperature electronic contribution to C, establish that the parent Ce alloy may be classified as a concentrated Kondo system. It is clear from the values of θ$_p$ that the strength of the Kondo effect at higher temperatures is nearly unaffected by initial substitutions of La (<1.0), whereas the weakening of the Kondo effect caused by an increase of unit-cell volume is realised only for higher doping of La. It may be added that there is a deviation from the high temperature Curie-Weiss behavior at lower temperatures presumably due to crystal-field effects. There is no ferromagnetic impurity contribution at low temperatures, as the isothermal magnetization is found to be a linear function of magnetic field.

Summarising, the present results establish that the compound Ce$_2$CoSi$_3$ is a non-magnetic concentrated Kondo system. The transformation from Kondo-lattice to single-ion Kondo behavior is investigated by the substitution of La for Ce in this compound. A notable finding is that, for x= 0.25, we observe linear T-dependence of low temperature resistivity, a feature which may characterise this composition as a NFL; it is worthwhile to extend the measurements to low temperatures (below 1 K) to probe whether this NFL behavior persists in such a range as well. Generally speaking, in non-magnetic Ce-based Kondo lattices, La substitution tends to drive Ce towards magnetic ordering following the well-known relationship between unit-cell volume and the Kondo effect and magnetic-coupling strengths [16]. In the present (parent) Ce compound, the strength of the Kondo interaction is so large (as indicated by Curie-Weiss parameter) that the lattice expansion caused by La substitution is not sufficient to cause magnetic ordering. From the observation of NFL behavior in resistivity for x= 0.25, we infer that this alloy can be located across the border separating Fermi-liquids and magnetic ordering regimes in the Doniach’s magnetic phase diagram [16]. Thus, this composition may be near the quantum critical-point and therefore the magnetic fluctuations presumably lead to non-Fermi-liquid properties [17]. We also performed ρ measurements with the application of H and we note that H does not influence linear temperature dependence of resistivity above 4.2 K, similar to the behavior of U$_{0.9}$Th$_{0.1}$ThBe$_{13}$ (Ref. 18). However, unlike the situation in this U alloy, the magnetoresistance, MR (till 70 kOe) at 4.2 K is found to be positive with a magnitude of less than 1%. It is possible that the positive MR results from Kondo coherence effects in these Ce alloys. It is of interest to extend MR measurements to very low temperatures (<1 K) in order to see whether Fermi-liquid behavior can be restored by the application of magnetic field, an information which will be extremely valuable to explore possible role of quadrupolar Kondo effect to result in NFL behavior [18]. We have reported in the past similar quasi-linear T dependence of resistivity in a stoichiometric compound, CeIr$_2$Ge$_2$ (Ref. 19). The understanding of such class of alloys in general is a challenge in condensed matter physics [20].

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Fig. 1
Fig. 3
$C / T \ (J / \text{mol} K^2)$

$T^2 (K^2)$

$\text{Ce}_{2-x} \text{La}_x \text{CoSi}_3$

$x = 0$

$x = 0.25$

$x = 0.5$

$x = 1$

$x = 1.5$

Fig. 4
Fig. 5

$\chi^{-1}$ (Ce mole/emu) vs $T$ (K) for $\text{Ce}_{2-x}\text{La}_x\text{CoSi}_3$ with different compositions $x = 0.0, 0.25, 0.5, 1.0, 1.5$. 

$\text{Ce}_{2-x}\text{La}_x\text{CoSi}_3$