PHYSICAL REVIEW B VOLUME 52, NUMBER 6 1 AUGUST 1995-II

$CeCoAl_4$: An incommensurate antiferromagnet

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(Received 13 March 1995)

The orthorhombic compound $CeCoAl_4$ orders antiferromagnetically at a relatively high Néel temperature T_N of 13 K. The resistivity of $CeCoAl_4$ shows a sharp increase near the magnetic transition before decreasing with temperature below 12 K. We believe that such behavior is due to the energy gaps induced by the incommensurate antiferromagnetic order. We have also studied the solid solutions $La_xCe_{1-x}CoAl_4$ for $x = 0.1$ and 0.2 and $CeCo_{1-y}T_yAl_4$ for T=Ni, Cu, and Pd. The crystal structure changes to $YNiAl_4$-type even at low values of y ($y \approx 0.1$ and T=Ni and Pd). We find that T_N decreases when La or Cu is substituted for Ce and Co, respectively. The sharp increase in the resistivity near T_N in $CeCoAl_4$ is almost smeared out in these pseudoternaries.

The isostoichiometric compounds $CeCoAl_4$ and $CeNiAl_4$ are both orthorhombic but belong to two different space groups. The difference arises due to the dissimilar stacking arrangement of the atoms in the crystal lattice. $CeCoAl_4$ has the $LaCoAl_4$-type structure, space group *Pmma* and $CeNiAl_4$ crystallizes in the $YNiAl_4$-type structure, space group *Cmcm*. Quite often isostoichiometric compounds of Ce with Co and Ni, respectively, have the same crystal structure and show similar magnetic behavior. $CeNiAl_4$ has been reported to be a nonmagnetic dense Kondo system with a Kondo temperature, T_K, of 76 K and an electronic specific heat coefficient, γ, of about 200 mJ/mol K^2.[1,2] In view of the difference in the configuration of the atoms in the two compounds, it is of interest to study the magnetic behavior of Ce in $CeCoAl_4$. We find that in contrast to nonmagnetic $CeNiAl_4$, $CeCoAl_4$ orders antiferromagnetically at a relatively high Néel temperature, T_N, of 13 K. The magnetic transition is associated with the Ce ions which show normal trivalent behavior. The properties of the nonmagnetic reference compound $LaCoAl_4$ were also studied for comparison. The effect of replacing Co by small amounts of Ni, Ru, Pd, Rh, and Cu and that of Ce by La was also investigated.

The alloys were made by melting together the constituents taken in proper ratio by weight in an arc furnace in an inert atmosphere of argon. The alloy buttons were repeatedly melted to ensure proper mixing. Weight losses during the melting were negligible. Powder x-ray-diffraction patterns on the as-cast alloys using Cu $K\alpha$ radiation were recorded to check for single phase formation. Magnetization was measured on the Quantum Design Superconducting quantum interference device (model MPMS) magnetometer. The low-temperature heat capacity (using the semiadiabatic heat-pulse method) and the four probe dc electrical resistivity were measured on the home built automated setups.

The x-ray-diffraction patterns of our as-cast samples $RCoAl_4$ (R=La and Ce) are similar and they could be indexed on the basis of an orthorhombic lattice. The lattice parameters a, b, and c are 7.701 and 7.680 Å, 4.082 and 4.063 Å, and 7.023 and 6.931 Å for the La and Ce compound, respectively. Our values for $LaCoAl_4$ are in excellent agreement with those listed in the literature.[3] The basic building blocks of both $RCoAl_4$ (R=La, Ce, and Pr) (Ref. 4) and $RNiAl_4$ (R=Ce to Lu) (Ref. 5) compounds are $MgCuAl_2$-type slabs. In $RNiAl_4$ these slabs are cut in such a way that there are R atoms at the interface with layers of Al atoms between the interfaces. On the other hand, in $RCoAl_4$ compounds the stacking arrangement of the $MgCuAl_2$-type slabs is such that there are Co atoms at the interface.

The magnetic susceptibility of $LaCoAl_4$ is practically temperature independent between 300 and 80 K and has a value of 6×10^{-5} emu/mol. This shows clearly that the Co atoms are nonmagnetic and that the Co $3d$ bands are filled due to the electron transfer. Below 80 K, the susceptibility shows a mild upturn and reaches a value of 8×10^{-5} emu/mol at 25 K and 12×10^{-5} at 5 K. This increase in the susceptibility may be due to the presence of small amount of magnetic impurities like, for example, magnetic rate earths in the starting material La. The susceptibility of $CeCoAl_4$ measured in a field of 2 kOe is shown in Fig. 1. A sharp cusp in the susceptibility occurs at 13 K and it indicates an antiferromagnetic transition. From the linear portion of the inverse susceptibility versus temperature an effective moment of 2.45 μ_B is obtained which is close to the free trivalent ion value of 2.54 μ_B. The magnetic ordering is, therefore, associated with the Ce ions while the Co sublattice is nonmagnetic. It is observed that the Néel temperature of $CeCoAl_4$ is reduced by about 1 K when the applied field is increased to 50 kOe (see inset of Fig. 1). Such a behavior is expected as the external magnetic field will not favor the antiferromagnetic coupling of the magnetic moments.

The electrical resistivity of $CeCoAl_4$ plotted in Fig. 2 shows an interesting behavior. Normally the resistivity of a rare-earth intermetallic decreases with a sharp change of slope at the magnetic ordering temperature as the scattering of the conduction electrons by the randomly oriented rare-earth spins decreases due to the ordering of the magnetic moments below the magnetic transition.

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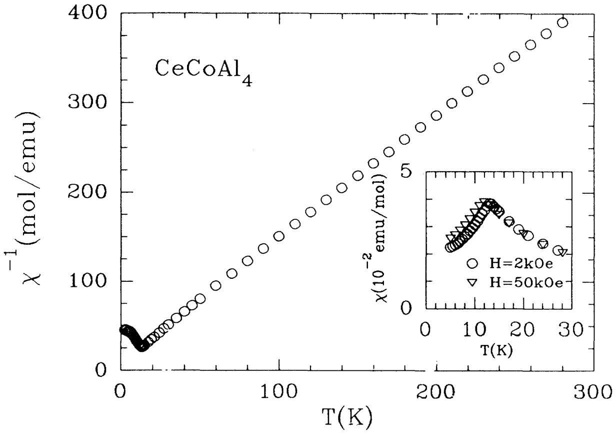

FIG. 1. The inverse susceptibility of CeCoAl$_4$ between 5 and 280 K. The inset shows the low-temperature susceptibility in external magnetic fields of 2 and 50 kOe, respectively.

But in CeCoAl$_4$ the resistivity shows a jump across the Néel temperature. It increases just below 14 K and peaks at 12 K before decreasing at lower temperatures. Such a feature is not seen in LaCoAl$_4$ and we believe that it arises from the energy gaps due to the formation of superlattice zone boundaries induced by the incommensurate antiferromagnetic order in CeCoAl$_4$. The periodic variation of the ionic moments which is incommensurate with the lattice introduces additional planes of discontinuity in the energy dispersion of conduction electrons which can give rise to an anomalous temperature dependence of the electrical resistivity if the gap cuts the Fermi surface or occurs in its vicinity.[6–8] Such anomalies have been observed in pure heavy rare-earth metals[9] and also in some intermetallic compounds.[10,11] Above the Néel temperature the resistivity of CeCoAl$_4$ shows the normal metallic behavior. In particular, the resistivity does not exhibit a region of negative slope associated with the Kondo effect. The resistivity of LaCoAl$_4$ is also plotted in Fig. 2. It is possible that our values of resistivity do not represent the intrinsic magnitude of this quantity due to possible microcracks which may be sample dependent and uncertainty in the geometrical factor.

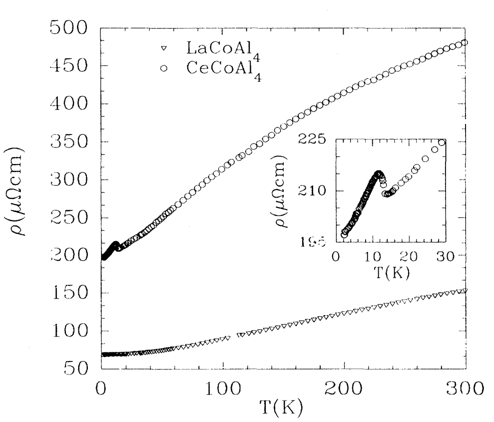

FIG. 2. The resistivity of CeCoAl$_4$ and LaCoAl$_4$ between 2 to 300 K. The inset shows the resistivity of CeCoAl$_4$ near the antiferromagnetic transition on an expanded scale.

The heat capacity of CeCoAl$_4$ and the nonmagnetic reference compound LaCoAl$_4$ is plotted in Fig. 3. An anomaly in the heat capacity, C, with a peak height of 13 J/mol K close to 13 K is observed and it arises due to the magnetic ordering of Ce ions. Interestingly, the linear extrapolation of the C/T versus T^2 plot in the paramagnetic region gives a C/T value of 230 mJ/mol K^2 at $T=0$ K. Such large values of the Sommerfeld coefficient, γ, are typically found in the rare-earth and actinide based heavy fermion materials.[12] But it has been shown in the literature[13,14] that unless all possible contributions to the total heat capacity in the paramagnetic state, such as Schottky heat capacity due to crystal-field split levels, etc. are first subtracted, one may obtain erroneously large values of C/T at $T=0$ K if the extrapolation is made from temperatures 10 K and above. Since the resistivity of CeCoAl$_4$ does not show any Kondo-like temperature dependence which is the hallmark of heavy fermion behavior, it is quite likely that the large extrapolated value of C/T at $T=0$ K is not truly of electronic origin. In order to estimate the entropy associated with the magnetic ordering we have assumed that the background conduction electron and the phonon heat capacity is the same as that of LaCoAl$_4$ and taken $C/T=0$ at 0 K for CeCoAl$_4$. We obtain a value of 5.9 J/mol K for the entropy up to 13.2 K, which exceeds slightly the theoretical value of R ln2 (=5.76 J/mol K) for a doublet ground state. However, since we have not subtracted the $4f$ contribution to the electronic heat capacity which for a normal Ce compound is of the order of 10 mJ/mol K^2, our value is an overestimate and the actual magnetic entropy should thus be very nearly equal to R ln2.

The marked difference in the magnetic behavior of CeCoAl$_4$ and CeNiAl$_4$ and the occurrence of an incommensurate antiferromagnetic transition in the former as inferred from resistivity data, prompted us to study the

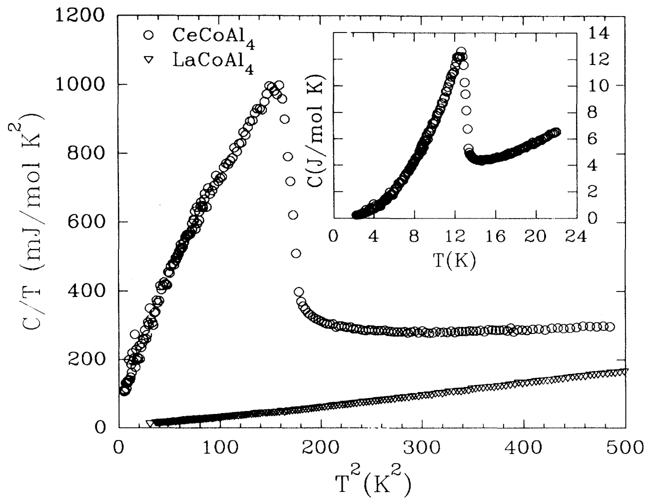

FIG. 3. The heat capacity plotted as C/T versus T^2 of CeCoAl$_4$ and LaCoAl$_4$. The inset shows the plot of C versus T of CeCoAl$_4$.

effect of replacing Co by Ni and Ce by La in $CeCoAl_4$. Our interest was to investigate the extent of single phase, homogeneous phase regions in the $CeCo_{1-x}Ni_xAl_4$ psuedoternary alloys and how Ni and La substitution would affect the behavior of resistivity in the vicinity of the Néel temperature. To our surprise, we find that a structural transformation to $YNiAl_4$ type takes place at rather low Ni substitution for Co. For example, even in $CeCo_{0.95}Ni_{0.05}Al_4$ the x-ray-diffraction pattern shows lines belonging to $CeNiAl_4$ phase (with slightly different lattice parameters) along with the diffraction lines due to $CeAl_2$ phase. The most intense lines of $CeAl_2$ are faintly present in $CeCo_{0.9}Ni_{0.1}Al_4$. At a higher Ni concentration in $CeCo_{0.75}Ni_{0.25}Al_4$, the diffraction pattern consists only of lines belonging to $CeNiAl_4$ phase. The relative instability of $LaCoAl_4$-type structure to Ni substitution appears to be rather general as $PrCo_{0.9}Ni_{0.1}Al_4$ shows similar behavior. It may be mentioned here that for the purpose of intercomparison we also made the parent alloys $CeNiAl_4$, $PrNiAl_4$, and $PrCoAl_4$. Other substituents with T=Rh, Ru, Pd, and Cu were also tried in $CeCo_{0.9}T_{0.1}Al_4$. With Rh and Ru, we find a predominant $CeAl_2$ phase but $CeCo_{0.9}Pd_{0.1}Al_4$ is single phase isostructural with $CeNiAl_4$. On the other hand, the parent structure is retained with Cu substitution and single phase alloys are obtained at least up to $CeCo_{0.9}Cu_{0.1}Al_4$. These observations are nicely corroborated by the susceptibility and resistivity data.

Figure 4 shows the susceptibility, χ, of $CeCo_{0.9}Cu_{0.1}Al_4$ and χ^{-1} of $CeCo_{0.9}Ni_{0.1}Al_4$. The temperature dependence of inverse susceptibility and its magnitude in $CeCo_{0.9}Ni_{0.1}Al_4$ is similar to that of $CeNiAl_4$ (see Fig. 3 of Ref. 1). A least-squares fit of the data above 80 K to the expression $\chi=c/(T-\theta_p)$ gives an effective paramagnetic moment, μ_{eff}, of 2.80 μ_B and paramagnetic Curie temperature, θ_p, of -250 K. For $CeNiAl_4$ the corresponding values are 2.68 μ_B and -172 K. The μ_{eff} values exceed the free trivalent ion value of 2.54 μ_B. A large negative value of θ_p is generally observed in valence fluctuating and Kondo lattice compounds and the relations $T_K \approx |\theta_p|/2$,[15] and $|\theta_p|/4$,[16] have been proposed in the literature, where T_K is the Kondo temperature. A more negative θ_p in $CeCo_{0.9}Ni_{0.1}Al_4$ indicates that the characteristic temperature, T_K, associated with the $4f$-shell instability is larger than in $CeNiAl_4$. Electrical resistivity measurements shown in Fig. 5 support such a conclusion. The resistivity of $CeNiAl_4$ is very similar to the earlier reported behavior in the literature.[1] The resistivity initially increases below 300 K, shows a broad maximum, and then decreases at low temperatures. The position of the maximum is dependent on T_K. In $CeCo_{0.9}Ni_{0.1}Al_4$ the resistivity does not exhibit any maximum below 300 K and most probably it has shifted to above 300 K, which would be in accord with the more negative θ_p value.

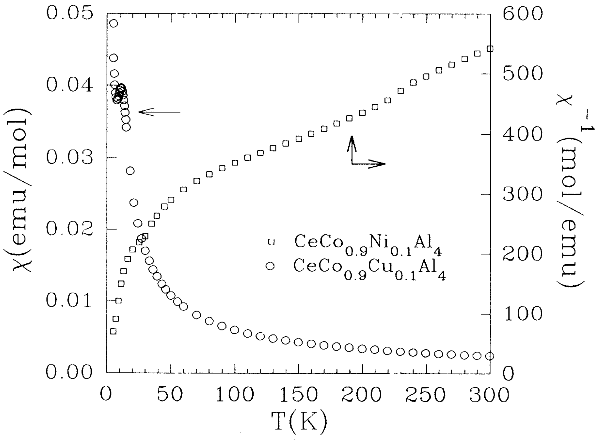

FIG. 4. The inverse susceptibility of $CeCo_{0.9}Ni_{0.1}Al_4$ and the susceptibility of $CeCo_{0.9}Cu_{0.1}Al_4$ between 5 and 300 K.

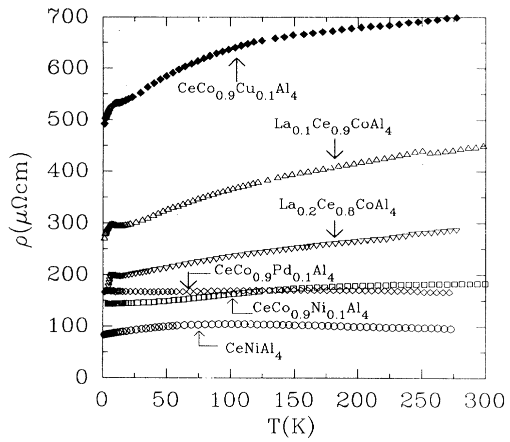

FIG. 5. The resistivity of $La_xCe_{1-x}CoAl_4$ (x=0.1 and 0.2) and $CeCo_{1-y}T_yAl_4$ (T=Cu, Ni, and Pd for y=0.1 and T=Ni for y=1).

The pseudoternary alloys containing Cu and La as substituents show magnetic ordering at temperatures lower than that of the parent $CeCoAl_4$. For alloys containing La that is expected as La substitution leads to magnetic dilution and would, therefore, reduce the magnetic ordering temperature. The susceptibility of $CeCo_{0.9}Cu_{0.1}Al_4$ (Fig. 4) shows a broad cusp centered at 11 K which is 2 K lower than the T_N of $CeCoAl_4$. The susceptibility rises further at lower temperatures and this rise may be due to a small impurity phase, undetected in the x-ray-diffraction pattern. The peculiar feature of the resistivity seen in pure $CeCoAl_4$ at the magnetic transition is severely modified in the pseudoternaries with the same structure (Fig. 5). The sharp upturn in the resistivity has broadened in $La_{0.1}Ce_{0.9}CoAl_4$ and occurs at lower temperature and practically disappeared in $CeCo_{0.9}Cu_{0.1}Al_4$ and $La_{0.2}Ce_{0.8}CoAl_4$. Changes in the lattice volume due to La and Cu substitution and possibly in the band electron density of states would obviously affect the position of the Fermi level and as a consequence the relative position of the energy gap due to the incommensurate magnetic order.

We thank R. Vijayaraghavan for his keen interest in this work and for his encouragement.

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