

Kondo-lattice behavior and multiple characteristic temperatures in CeIr_2Ge_2

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(Received 11 July 1996; revised manuscript received 4 November 1996)

The results of electrical-resistivity ρ measurements (1.4–300 K) on the alloys, $\text{Ce}_{1-x}\text{La}_x\text{Ir}_2\text{Ge}_2$ ($0 \leq x \leq 1$), $\text{CeIr}_{2-x}(\text{Rh,Pt})_x\text{Ge}_2$ ($x=0.2$ and 0.4), and $\text{CeIr}_2\text{Ge}_{2-x}(\text{Si,Sn})_x$ ($x=0.2$ and 0.4), are reported in order to understand the Kondo effect in CeIr_2Ge_2 . There is a significant decrease in ρ as the temperature is lowered from 100 to 4.2 K for $x = 0.0$. This feature disappears for a small replacement of Ce by La ($x = 0.3$), thereby resulting in a single-ion Kondo effect for higher values of x . This finding establishes that the temperature T_{coh} , characterizing the coherent scattering among the Kondo centers for $x=0$ is as large as about 100 K. The coherent scattering is not destroyed by small substitutions at the Ir or Ge site. The observed sensitivity of this coherence effect to a small disruption of Ce sublattice periodicity alone by La substitution is uncommon among trivalent Ce alloys. Such a large T_{coh} value enables us to emphasize the need to invoke three characteristic temperatures for nonmagnetic Kondo lattices. [S0163-1829(97)04806-6]

Depending upon the degree of $4f$ hybridization with the conduction band, the nature of the ground state of Ce and other physical characteristics have been found to vary from one compound to the other. As a result, the interest in Ce compounds remains unabated. It is a well-known fact¹⁻³ that, in many Kondo lattices, the coherent scattering among the Kondo centers as the temperature is lowered results in a marked drop of electrical resistance (ρ) below a characteristic temperature (T_{coh}). Most of the Ce compounds, in which Ce is nearly trivalent (that is, weakly hybridized systems), are characterized by low T_{coh} values (less than 20 K). Generally, one sees Fermi-liquid characteristics below a certain temperature T_{coh}^* , which is lower than T_{coh} . Several years ago, Anderson⁴ and Coleman⁵ put forward the idea that the temperature, T_{coh}^* , below which the quasiparticle bands arise, differ from the single-ion spin-fluctuation temperature by a factor of $1/(2j+1)$ (where $j=5/2$ for fully degenerate trivalent Ce ion). This idea was subsequently discussed to describe the ρ behavior of the mixed-valent compound CePd_3 by Lawrence *et al.*⁶ However there were no further experimental reports aimed at probing whether the nonmagnetic Kondo lattices, particularly the alloys containing trivalent Ce ions, are characterized by multiple characteristic energies, viz., T_{coh}^* , T_{coh} and T_K (where T_K is the single-ion Kondo temperature). One of the reasons for this situation could be that the value of T_{coh} is generally well below 20 K in most of the trivalent Ce alloys and hence the temperature window available to address this question is rather limited. Therefore, there is a need to identify trivalent Ce compounds in which the onset of the coherence effect is pushed to higher temperatures. In this respect, the recently discovered CeFeGe_3 (Refs. 7–10) in which T_{coh} is about 100 K is of significance. In this article, we present the results of ρ measurements on a nonmagnetic Ce compound, viz., CeIr_2Ge_2 , (Refs. 11–13) and some of its pseudoternary alloys. The results establish the onset of Kondo coherent scattering near

100 K in this compound. Our results suggest that these three characteristic energies are widely different in this compound and, apparently, there is no simple relationship between T_{coh}^* and T_K . The other observations to be emphasized are (i) The amount of isovalent ion (viz., La) required to suppress the coherence peak in ρ is unusually small for a trivalent Ce compound with such a large value of T_{coh} and (ii) ρ exhibits quasilinear dependence on temperature below about 11 K (which is referred to as T_{coh}^* as far as this compound is concerned in this article) rather than the quadratic dependence.

The samples, $\text{Ce}_{1-x}\text{La}_x\text{Ir}_2\text{Ge}_2$ ($x=0.0, 0.1, 0.2, 0.3, 0.5, 0.7, 0.9$, and 1.0), $\text{CeIr}_{2-x}(\text{Rh,Pt})_x\text{Ge}_2$ ($x=0.2$ and 0.4) and $\text{CeIr}_2\text{Ge}_{2-x}(\text{Si,Sn})_x$ ($x=0.2$ and 0.4), were prepared by arc melting. Some of these alloys were subjected to homogenization in evacuated sealed quartz tubes at 800 °C for week and we noticed that the resistivity of the homogenized ingots is significantly higher than that of the as-cast specimens. This implies that homogenization creates crystallographic imperfections and hence we restricted our studies reported here to as-cast specimens. The samples were characterized by x-ray diffraction and the lines could be indexed on the basis of CaBe_2Ge_2 -type tetragonal structure. The ρ measurements were performed (1.4–300 K) by a conventional four-probe method using a silver paint for making electrical contacts; due to microcracks in the samples, no comparison of the values of ρ may be made among these alloys. Ce L_{III} -edge x-ray-absorption measurements for CeIr_2Ge_2 were performed at selected temperatures between 10 and 300 K at the EXAFS-II beamline of HASYLAB (DESY, Hamburg).

The results of ρ measurements normalized to respective 300 K values are shown in Fig. 1. In the case of CeIr_2Ge_2 , there is a small increase of ρ with decreasing temperature (T) down to about 100 K, following which there is a gradual fall from about 0.39 m Ω cm at 100 K to about 0.23 m Ω cm at 2 K. Thus there is a reduction of ρ by about 40%. It may be remarked that Mathur and Frost¹² have reported a very

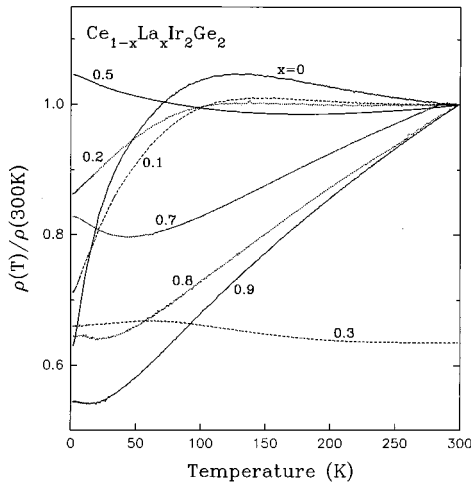


FIG. 1. The electrical resistivity (ρ) as a function of temperature (T) in the alloys, $\text{Ce}_{1-x}\text{La}_x\text{Ir}_2\text{Ge}_2$, normalized to respective 300 K values. The data for $x=0.3$ is shifted down on the vertical axis for the sake of clarity.

small value of 0.05 for ρ (4.2 K)/ ρ (300 K) on the best platelets of this compound. The enhancement of this ratio in our alloy (to about 0.6) is presumably due to strong grain-boundary effects in the way we have prepared these alloys. For this reason, no significance may be attached to absolute values of this ratio in all our specimens, though qualitative conclusions drawn on the basis of the trends in these values from one composition to the other are still valid. Such large drops of ρ below 100 K cannot be explained in terms of crystal-field effects and we have therefore proposed the existence of Kondo coherence effects around 100 K (Ref. 13). In order to establish this interpretation, one should look for the features in the ρ data when the Ce sublattice is diluted with a nonmagnetic rare-earth ion. Thus the ρ data of La-substituted alloys shown in Fig. 1 are conclusive. For $x=0.1$, ρ is nearly independent of temperature above 100 K and it falls by about 27% as the temperature is lowered to 2 K; for $x=0.2$, the corresponding drop is about 15%. For $x=0.3$, the low-temperature drop is suppressed and the decrease in ρ is less than 1% below 60 K; $d\rho/dT$ is negative in the temperature range 60–300 K; these features are characteristic of single-ion Kondo effect. Further substitution of La, viz., $x=0.5$, results in complete modification of the overall features and the low temperature drop is no longer observed, instead there is a broad minimum around 180 K with a rise of about 6% from 180 to 2 K. For $x=0.7$, the lattice contribution dominates above 50 K, resulting in the Kondo minimum at about 45 K; the percentage increase in low temperature ρ is less than 3%. For $x=0.8$, the overall features are the same, except that the minimum is shifted to 30 K and the magnitude of the low-temperature rise is around 1%. For $x=0.9$, the Kondo minimum is apparently absent, as, following the composition dependence of the percentage increase of low-temperature rise, the expected upturn should be extremely small.

From the above experimental observations, it is clear that the destruction of the periodicity of the Ce sublattice by the substitution of La suppresses the drop of ρ below 100 K. This suppression of the low-temperature fall with La substi-

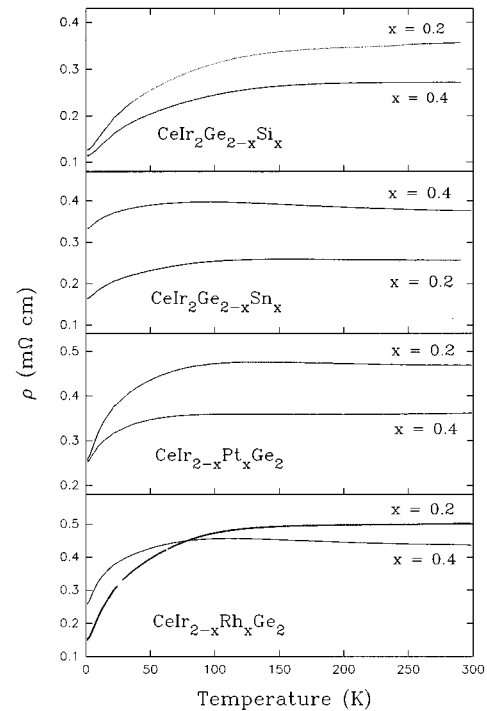


FIG. 2. The electrical resistivity as a function of temperature for several alloys of CeIr_2Ge_2 substituted for Ir and Ge.

tion can be explained only if one assumes that this drop arises from the coherent scattering among the Kondo centers. Such a situation involving a disruption of the Ce periodicity by a small ($x=0.3$) isovalent ionic substitution is not frequently met with in a Ce-based Kondo lattice with such a large Kondo coherence temperature in the nearly trivalent limit of Ce. Even in the series, $\text{Ce}_{1-x}\text{La}_x\text{FeGe}_3$, a larger concentration of La ($x=0.5$) is required to destroy coherence effects^{9,10} and, in this sense, the behavior of CeIr_2Ge_2 appears to be unusual. We have also probed the sensitivity of the coherence-derived peak in ρ to small substitutions at the non-Ce site (Rh or Pt for Ir; Si or Sn for Ge), the results of which are shown in Fig. 2. It is to be noted that this feature persists in all these alloys. In fact, initial substitutions ($x=0.2$) of Rh and Si result in a drop by 70% and of Pt by about 45%, thus making the coherence effect in fact more prominent; further increase of x to 0.4 appears to change $\rho(T)/\rho(300\text{ K})$ towards the original value. Sn substitution apparently does not significantly alter a coherence-related drop of ρ . From these observations, it can be concluded that the chemical pressure, both positive or negative, involving isoelectronic as well as nonisoelectronic substitutions at the Ir/Ge site does not result in the destruction of the coherence effect. The substitutional effect at the Ce site by La, to the contrary, establishes that the periodicity of the Ce sublattice is crucial for the coherence effect at such a high temperature.

It may be recalled that the coherence effect around 100 K has been known⁶ in mixed-valent CePd_3 , in which case a distinct deviation of the lattice constants from the lanthanide contraction characteristic of the intermediate valence for Ce is well known. In contrast, in CeIr_2Ge_2 , the lattice constants follow¹¹ lanthanide contraction at room temperature as if Ce is more trivalent in this compound compared to CePd_3 . In order to address this question in a straightforward manner,

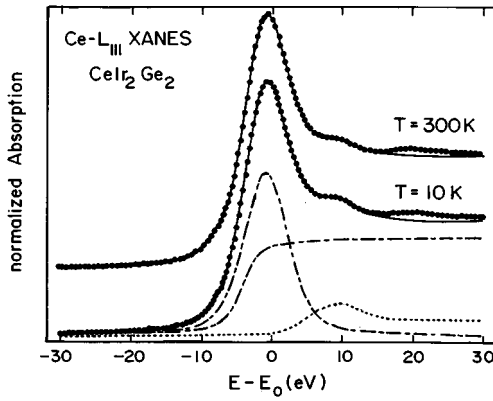


FIG. 3. Ce L_{III} -edge spectra of CeIr_2Ge_2 at 300 and 10 K. For Ce^{3+} , the white line (a Lorentzian) and the edge (an arctan function) are also shown by long-dashed lines. The Ce^{4+} subspectrum (short-dashed) shown is the sum of these two components. E_0 corresponds to the white line of a reference (CeF_3).

we show the Ce L_{III} -edge spectra of CeIr_2Ge_2 at 10 and 300 K in Fig. 3. In this spectroscopy, one observes a pronounced absorption peak (white line) at the edge position corresponding to a $2p_{3/2}$ to $5d$ transition. In metallic Ce systems with tetravalent admixture, one observes a double-peaked edge profile one each from Ce^{3+} and Ce^{4+} in the initial state, shifted by nearly 10 eV. The valency is generally derived from the relative amount of Ce^{3+} and Ce^{4+} edge profiles. In the present system, there is a prominent peak near E_0 , defined by the maximum absorption (white line) of the CeF_3 reference at 5725 eV and a small tetravalent component, shifted by about 10 eV to higher energy. From an usual line-shape analysis,¹⁴ we derive that the mean valence of Ce is 3.07 ± 0.02 and 3.1 ± 0.02 at 300 and 10 K, respectively. Thus these results establish that Ce is close to trivalency in this compound down to 10 K.

It is also of interest to compare the absolute values of Ce valency in CePd_3 and CeIr_2Ge_2 . A visual comparison of the spectra of CePd_3 (Ref. 15) suggests that the tetravalent component in CePd_3 is comparatively higher. The heat-capacity (C) and magnetic-susceptibility (χ) results¹³ are also consistent with these conclusions. The value of the linear term (γ) obtained from the plot of C/T versus T^2 below 20 K is about 130 mJ/mol K^2 for CeIr_2Ge_2 , which may be compared with 40 mJ/mol K^2 for CePd_3 (Ref. 16). The relatively large value for the former suggests that the $4f$ orbital of Ce in the Ir sample is more localized compared with that in CePd_3 . From the $4f$ contribution (χ_{4f}) to χ , obtained after subtracting χ (300 K) of LaIr_2Ge_2 , the values of μ_{eff} and θ_p for $x=0.0$ are found to be $2.5\mu_B$ and -160 K, respectively, from the linear region of the plot of inverse χ versus T above 200 K. The value of the effective moment proves that Ce ions are trivalent.

We now pay some attention to an observation in the low-temperature ρ data. We notice that ρ at low temperatures exhibits a quasilinear behavior in CeIr_2Ge_2 , instead of the expected quadratic behavior (see Fig. 4). The low-temperature ρ data are plotted for three compositions in two different ways in Fig. 4 to highlight this point. It appears that ρ varies with $T^{1.2}$ over a wide temperature range (up to 11 K), in contrast to near-quadratic behavior only till 4 K. The

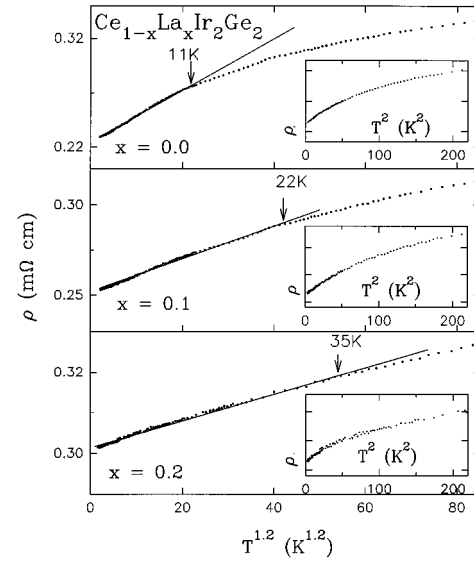


FIG. 4. The electrical resistivity (ρ) versus $T^{1.2}$ at low temperatures for three alloys of the series, $\text{Ce}_{1-x}\text{La}_x\text{Ir}_2\text{Ge}_2$. In the insets, the data at lower temperatures are plotted as a function of the square of temperature. The continuous lines drawn through the data points show the linear region.

range of quasilinear behavior extends to about 22 and 35 K for $x=0.1$ and 0.2 , respectively, and apparently this feature persists (see Fig. 1) even in the Kondo-impurity regime, e.g., $x=0.5$, up to at least 30 K. We also attempted to subtract the lattice contribution employing the values of LaIr_2Ge_2 and we noted that the quasilinear variation extends to a few more degrees Kelvin. We, however, do not show the $4f$ contribution to ρ thus obtained in the form of plots, as there is no systematic in the absolute values of ρ as stated earlier. It can be confidently stated that a non-Fermi-liquid behavior¹⁷ in ρ is demonstrated in a Kondo-lattice system with a high T_{coh} . The low-temperature divergence (non-Fermi-liquid behavior)^{17,18} in C is however not noted,¹⁰ instead C/T varies linearly with T^2 below 20 K as mentioned above. Though one is tempted to attribute the observed anomaly in ρ to small intrinsic crystallographic disorder possibly giving rise to a distribution¹⁹ in the single-ion Kondo temperature, the trends seen in the alloys substituted at Ir/Ge sites as argued below do not appear to support this idea. The $T^{1.2}$ dependence of ρ gets modified with the substitutions at Ge and Ir sites; below 7 K, Si and Rh substitutions restore T^2 dependence, while Pt and Sn substitutions result in $T^{1.5}$ dependence, thereby showing a tendency towards Fermi-liquid behavior; since these chemical substitutions naturally result in additional crystallographic disorder possibly resulting in a distribution of the T_K value, one should have observed more deviations from Fermi-liquid behavior in these substituted alloys. The findings to the contrary in the substituted alloys therefore suggest that the distribution in T_K resulting from possible crystallographic imperfections may not be the true cause of the anomaly in CeIr_2Ge_2 . At this juncture, it is to be noted that the low-temperature $T^{1.2}$ behavior observed²⁰ in the high-pressure phase of CePd_2Si_2 is being reproduced without the application of an external pressure in CeIr_2Ge_2 . Further systematic studies, extended to the millikelvin range on several substituted samples, are needed to throw more

light on the ground state, in view of the fact that the high-pressure phase of CePd₂Si₂ undergoes heavy fermion superconducting transition around 0.5 K.²⁰

From the above data, it is clear that there is a temperature (T_{coh}^*) below which one sees non-Fermi-liquid behavior and that the value of T_{coh}^* is far below T_{coh} . It is of interest to compare the values of T_{coh}^* and T_{coh} with that of T_K . As mentioned in this paper, the value of T_K given by θ_p is large. One can obtain^{8,21} a more precise value of T_K from that of χ at 2 K and it turns out to be 185 K. This value also agrees with that determined²¹ from γ data ($T_K=180$ K). While determining the value of T_K from $\chi(2$ K) and γ data, we have assumed $j=5/2$ in the relationship between these quantities.^{8,21} It is clear that the value of T_K is significantly larger than those of T_{coh}^* and T_{coh} . This finding implies that this Kondo lattice is characterized by three energies, T_{coh}^* , T_{coh} , and T_K . This conclusion is qualitatively consistent with the ideas discussed in Refs. 4–6. Quantitatively, the

value of T_{coh}^* for CeIr₂Ge₂ is less than half of the expected value, that is, $T_K/2j+1$. If one strictly defines T_{coh}^* as a temperature until which ρ exhibits quadratic temperature dependence (in which case $T_{\text{coh}}^* < 4$ K), then the deviation from the expected value is clearly still larger. This observation supports the opinion of Lawrence *et al.*⁶ that the two energies T_{coh}^* and T_K are not uniquely related and that the relationship appears to depend on various other details like crystal structure, band structure, etc.

To conclude, in the compound CeIr₂Ge₂, the onset of Kondo coherent scattering effect occurs at a rather high temperature (close to 100 K). This effect could be destroyed by an unusually small isovalent ionic substitution at the Ce site. Unlike other Kondo lattices, ρ apparently exhibits non-Fermi-liquid behavior below about 11 K. The large value of T_{coh} enables us to revive the idea⁶ of invoking multiple characteristic energies even in those Kondo lattices in which Ce valency is close to 3.

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