

Heavy Fermion Behaviour in $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$

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Dedicated to Dr. Bernard Chevalier on the occasion of his 60th birthday

The intermetallic compound $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$ (tetragonal Mo_2FeB_2 -type structure) has been investigated by magnetization (down to 1.8 K), electrical resistivity (ρ) and heat capacity (down to 0.5 K) measurements as a function of temperature (T). On the basis of these data, it is concluded that this compound is a heavy-fermion with a Kondo temperature in the range 235 – 250 K. Fermi-liquid behaviour expected for Kondo lattices is obeyed for the low temperature ρ data, but the ratio of the coefficient of the T^2 term in the electrical resistivity to the square of the linear coefficient of the heat capacity is apparently low compared to the ‘universal ratio’ known for other cerium compounds, as though there is a breakdown of the Kadowaki-Woods relation in this compound. The value of this ratio falls in the range known for many intermediate-valent ytterbium compounds.

Key words: $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$, Heavy Fermion, Kadowaki-Woods Relation

Introduction

In the field of ‘Strongly Correlated Electron Systems’, the rare earth (R) intermetallics, particularly those containing cerium, have been at the centre stage of active research. In this respect, the family of ternary intermetallic compounds R_2T_2X (R = rare earth or actinide; T = late transition metal; X = element of the 3rd, 4th or 5th main group) with the tetragonal Mo_2FeB_2 -type structure (space group $P4/mbm$) has attracted some attention during the last ten years [1, 2] with respect to its crystallographic, magnetic and electrical properties. The cadmium-based compounds, however, did not receive much attention possibly because of the difficulties in preparing these samples.

In this article, we focus on the rare earth series $R_2\text{Ni}_2\text{Cd}$. A projection of the $R_2\text{Ni}_2\text{Cd}$ structure is shown in Fig. 1. The structure is a 1:1 intergrowth version of slightly distorted AlB_2 and CsCl related slabs of compositions $R\text{Ni}_2$ and RCd . Magnetic ordering and mixed-valence characteristics have been found among the cerium compounds in this family. We now present the results of our DC magnetization (M), electrical resistivity (ρ) and heat capacity (C) investigations as a function of temperature (T) on $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$,

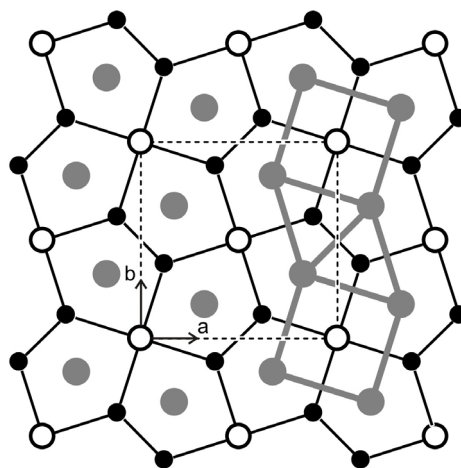


Fig. 1. View of the $\text{Ce}_2\text{Ni}_2\text{Cd}$ structure along the c direction. The two-dimensional Ni_2Cd network as well as the distorted AlB_2 and CsCl related slabs are emphasized.

on which only a preliminary M and ρ study had been published [3]. For a hitherto unknown reason, there are vacancies at the Ni site, generally resulting in the formation of off-stoichiometric compounds, $R_2\text{Ni}_{2-x}\text{Cd}$, with a very small homogeneity range close to $x = 0.12$. To minimize possible interference with the magnetic

data due to precipitation of excess Ni, we chose the optimum composition, $x = 0.12$. A notable reduction in the unit cell volume for the Ce compound in this series from the values expected on the basis of the lanthanide contraction is evident [4], thereby establishing strong Ce $4f$ hybridization. We considered it worthwhile to subject this system to further investigations to look for heavy-fermion behaviour. We have therefore carried out detailed studies on a freshly prepared sample of $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$.

Experimental Section

Starting materials for the preparation of $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$ were cerium ingots, nickel wire and a cadmium rod (all from Johnson Matthey, with stated purities better than 99.9 %) and the sample was prepared as discussed in Ref. [3]. Due to the low boiling temperature of cadmium, the sample was prepared in a tantalum tube with the starting components in the atomic ratio 2 : 1.88 : 1 sealed under an argon pressure of about 800 mbar. A high-frequency furnace was employed for this purpose. The tube was first heated under flowing argon with the maximum power of the high-frequency generator. The exothermic reaction between the three elements was visible by the occurrence of a heat flash. At that stage, the annealing temperature was lowered to 1100 K for a few minutes and the tube was subsequently annealed for 1 h at 900 K, resulting in a polycrystalline sample of $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$. The sample was characterized by X-ray diffraction as described in Ref. [3] using $\text{CuK}\alpha_1$ radiation ($a = 7.5567(8)$ and $c = 3.7514(6)$ Å). We found a very weak line near $2\theta = 28.5$ degrees, the position of which does not match with any of the known binary and ternary phases of Ce, Ni and Cd. It is therefore possible that this compound in the powder form has undergone slow surface oxidation, though it may be stable in the bulk form over a long period of time as stated in Ref. [4]. We also looked at the bulk form through a scanning electron microscope and found that the sample was homogeneous throughout the material with uniform composition and without evidence for any other phase (except some negligible islands of free Cd). This certified that there was no other magnetic impurity phase that could interfere with the interpretation of the results.

All the magnetic measurements were performed on the bulk form. The M measurements were performed in the temperature interval 1.8–300 K employing a commercial superconducting quantum interference device (SQUID) (Quantum Design, USA) in fields H of 5 and 100 kOe; isothermal M measurements were also performed at several temperatures employing a commercial vibrating sample magnetometer (VSM). Heat capacity measurements were performed with the Physical Property Measurements System (Quantum Design, USA) down to 0.5 K; the same equipment

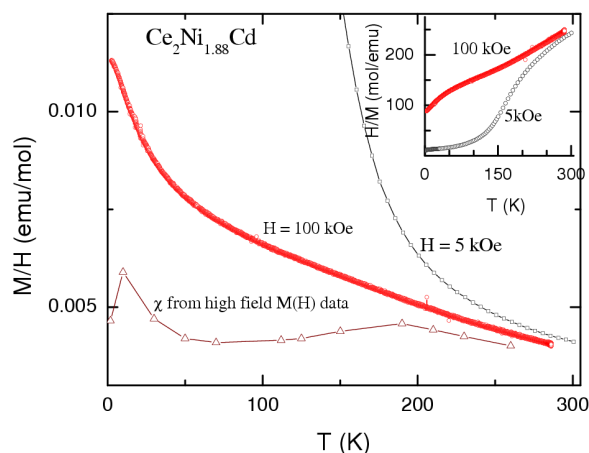


Fig. 2. (color online) Magnetization (M) divided by magnetic-field (H) as a function of temperature (T) for $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$ obtained in fields of $H = 5$ and 100 kOe. The magnetic susceptibility data derived from the high-field linear region in M - H plots of Fig. 3 are also shown. Inset shows H/M as a function of T .

was employed for measuring ρ by a conventional four-probe method employing silver paint for making electrical contacts of the leads with the sample.

Results and Discussion

The results of M measurements are shown in Fig. 2. It is distinctly clear from the inset of this figure that the linear variation of H/M extends over a wider temperature range (above 100 K) if the measurements are performed in high fields, say $H = 100$ kOe, whereas the linearity is restricted to the range 200 to 300 K for $H = 5$ kOe. The H/M values, though close, are not the same for these H values even at temperatures close to 250 K. Thus, there appears to be a weak ferromagnetic component (which could be suppressed by the application of very high magnetic fields) in addition to the main paramagnetic component in this material. Assuming that the high temperature linearity for $H = 100$ kOe represents Curie-Weiss behaviour, the value of the effective moment obtained ($2.62 \pm 0.02 \mu_B$) is very close to that expected for trivalent cerium; the value of the paramagnetic Curie temperature is about -150 K, which indicates strong $4f$ hybridization in the absence of magnetic ordering. For $H = 5$ kOe, as the temperature is lowered below 150 K, there is a dramatic upturn of M/H (due to the magnetic contribution), and this upturn is rather gradual for $H = 100$ kOe even at lower temperatures. Considering that this fea-

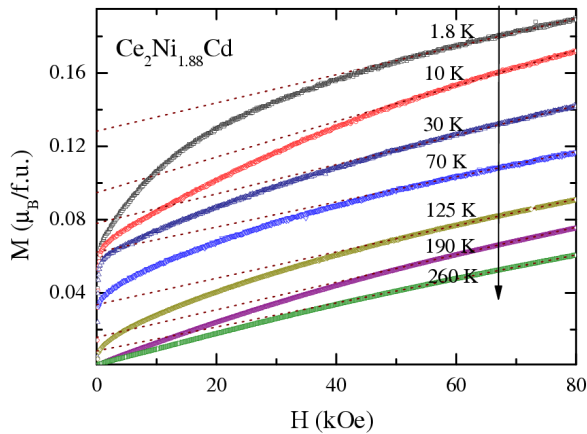


Fig. 3 (color online). Isothermal magnetization at selected temperatures for $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$. The dashed lines are drawn through the high-field linear region.

ture appears in freshly prepared bulk samples as well and that there is no magnetic impurity phase, this magnetism must arise from the nickel content. We are not able to resolve at present whether it arises from Ni at the grain boundaries with a spread in the magnetic ordering temperature (considering the absence of a well-defined λ anomaly in $C(T)$ in the temperature range of investigation as shown below) depending on the local coordination, or whether it is intrinsic to Ni atoms in the compound. It is possible that the magnetic transition temperature for Ni is marginally higher than 300 K (also considering the isothermal M behaviour shown in Fig. 3). We are however interested in understanding the heavy-fermion behaviour of Ce and pay attention to this issue only.

In order to obtain the intrinsic χ due to cerium, we have performed isothermal M measurements at selected temperatures with a VSM. We show typical curves in Fig. 3. It is distinctly clear from Fig. 3 that nonlinearity of the M - H plots extends to fairly high temperatures, and that there is a sharp rise for initial applications of magnetic field as the temperature is lowered, somewhat similar to that seen in Fig. 3 of Ref. [3]. The curves are essentially non-hysteretic. We would like to emphasize that we observed similar behaviour of the $M(H)$ curve even in the La analogue, and this gives credence to our view that the sharp rise arises from the Ni content. The same figure also depicts that, at high fields, the $M(H)$ plots are linear and nearly parallel at all temperatures. This supports our conclusion stated above that there is a Pauli-paramagnetic component superimposed over the ferromagnetic compo-

nent. It is apparent from the figure that the spontaneous magnetic moment obtained by linear extrapolation from high-field data gradually decreases with increasing temperature; this value, though small, is finite near 300 K, thereby endorsing that a weak ferromagnetic transition from Ni may occur near 300 K. From the linear region, we extracted the values of χ intrinsic to the paramagnetic part (attributable to cerium) at low temperatures, which are also plotted in Fig. 2. It is apparent that there is a broad maximum in $\chi(T)$ occurring around 200 K typical of strongly $4f$ -hybridized cerium compounds. The lone data point at 5 K, which is reproducible not only with the VSM, but also with the SQUID magnetometer, suggests the existence of another peak around this temperature the origin of which is not clear to us at present. We have obtained the value of the Kondo temperature $T_K = 235$ K from the value of intrinsic χ for $T \rightarrow 0$ (typically given by the value at 1.8 K) employing the relation [5]

$$T_K = \frac{(0.1026N(N^2 - 1)(g\mu_B)^2)}{(6k_B\chi_{1.8K})}.$$

Here N is degeneracy, which is taken as 6 in view of strong $4f$ hybridization as indicated by a large T_K ; other symbols have the usual meanings.

We have performed C measurements in the T interval 0.5 to 220 K in order to confirm the conclusions stated above. We do not find (Fig. 4a) any λ anomaly in the $C(T)$ plot in the temperature region of investigation which establishes that Ce is essentially non-magnetic down to 0.5 K. We have also taken C in the presence of a magnetic field of 50 kOe and we find that the $C(T)$ curve thus obtained overlaps perfectly well with that of zero-field in the entire temperature range indicating that the fraction and size of the ferromagnetic pockets, if it arises from grain boundaries, must be negligible. In order to infer heavy-fermion behaviour, we have plotted C/T versus T^2 below 10 K in the inset of Fig. 4a. The plot is linear down to nearly 2 K with a value of the linear coefficient (γ) of about 115 mJ/molK². The value of C/T increases to about 170 mJ/molK² at 0.5 K. These values establish that this compound is a heavy-fermion. From the value of the linear term in the range 2–10 K, we have estimated the value of T_K employing the relation [5]

$$T_K = \frac{WJ\pi R}{3\gamma}$$

(where R is the gas constant and $W = 0.1026 \times 4\pi$ is

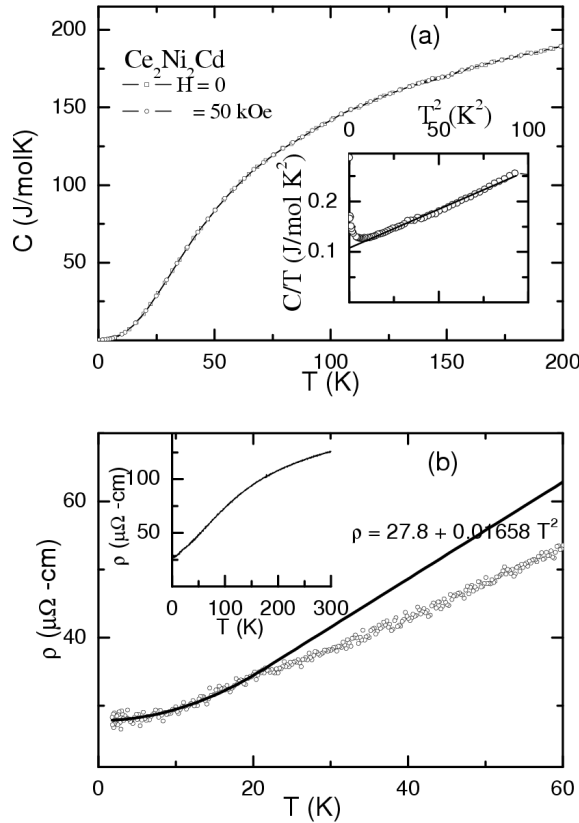


Fig. 4. (a) Heat capacity (C) (per mole of the compound) as a function of temperature (T) for $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$ in zero field and in a field of $H = 50$ kOe. The inset shows the plot of C/T versus T^2 . A straight line is drawn through the linear region in the inset. In the mainframe of (b), the electrical resistivity as a function of temperature is plotted below 60 K, whereas the data in the extended temperature range is shown in the inset; the continuous line is a fit to a quadratic expression below 20 K.

the Wilson number), which turns to be nearly 250 K. Here, it is assumed that $J = 5/2$, and the close agreement of this value of T_K with that obtained from the χ data establishes full degeneracy of trivalent Ce. This internal consistency offers support to the line of analysis of the M data, and the upturn of C/T below 2 K could be due to some degree of disorder.

The results of ρ measurements are shown in Fig. 4b. While the absolute values of ρ at high temperatures ($125 \mu\Omega \cdot \text{cm}$ at 300 K) are comparable to that reported in Ref. [3], the residual resistivity (value as $T \rightarrow 0$) is much smaller than that reported, which suggests that the present specimen is a better one. The shape of the $\rho(T)$ plot is similar to that known for mixed-valent compounds. The ρ exhibits T^2 de-

pendence below about 20 K typical of Fermi liquids, and the value of the T^2 coefficient turns out to be $0.01658 \mu\Omega \cdot \text{cm}/\text{K}^2$, in close agreement with that reported ($0.0056 (\mu\Omega \cdot \text{cm})/\text{K}^2$) earlier [3].

We now address the question of validity of the Kadowaki-Woods relation [6], a topic of interest in recent years [7–11]. It has been believed for quite a long time that, in the case of heavy-fermions behaving like Fermi-liquids, there is one universal ratio between the coefficient (A) of T^2 in electrical resistivity (ρ) and γ^2 , as brought out by Kadowaki and Woods [6]. That is, for a variety of strongly correlated f electron systems, $A/\gamma^2 = 1 \times 10^{-5} \mu\Omega \cdot \text{cm} \cdot \text{mol}^2 \cdot \text{K}^2 \cdot \text{mJ}^{-2}$. Very recently [7], this belief has been called into question for many of the Yb-based compounds with the value of this ratio being an order of magnitude smaller, as though there is another universal ratio. Kontani [10] theoretically established that N as well as the carrier density (n) play a role in determining the value of this ratio. Recently, Park *et al.* [11] confirmed this theoretical proposal on the basis of high-pressure experiments on mixed-valent YbCu_4In . It turned out that all the Yb compounds with an anomalously low ratio of A/γ^2 are strongly mixed-valent with a fully degenerate ground state, supporting the above proposal. However, such a breakdown was relatively unknown for Ce systems, with the exception of CeSn_3 [7] and CeNi_9Si_4 [8, 9], and it was established that this anomaly is single-ionic in nature and not due to any inter-site interactions [8], consistent with the above theoretical prediction [10]. Thus, it appears that there is a consensus that integral valent Ce or Yb compounds with a crystal-field split ground state (say, a doublet) should be characterized by a traditional value of A/γ^2 , whereas, in strongly f -hybridized systems, the value (without normalization to N and n) should fall in the range of the ‘second universal ratio’.

Interestingly, the above view was not sufficiently established for Ce-based systems and it is therefore of interest to explore the behaviour of the A/γ^2 ratio for the present compound, given that the ground state of Ce is fully degenerate due to strong $4f$ hybridization. Employing the values of γ and A obtained in this study, we arrive at a value of about $1.25 \times 10^{-6} \mu\Omega \cdot \text{cm} \cdot \text{mol}^2 \cdot \text{K}^2 \cdot \text{mJ}^{-2}$ for this ratio; if we use the value of A reported in Ref. [3], we arrive at a still smaller value. Thus, this finding apparently classifies this compound with those of the ‘second universal ratio’. It is however not clear whether one is misled to

this inference by a possible dominating contribution from conductivity across grain boundaries.

Summary

The present study firmly establishes that the compound, $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$, is a heavy-fermion with a Kondo temperature in the range 235 to 250 K, placing it in a strongly $4f$ -hybridized regime. Interestingly, the value of A/γ^2 is much smaller compared to many weakly $4f$ -hybridized Ce compounds, emphasizing the role of other factors (*e. g.* f orbital degeneracy and possible conductivity across grain boundary) in determining the Kadowaki-Woods ratio for Ce systems as well. Finally, we find that it is difficult to synthesize a specimen

of the material, $\text{Ce}_2\text{Ni}_{1.88}\text{Cd}$, without any weak ferromagnetic component and therefore this magnetism could be intrinsically arising for Ni in the compound, though one can not rule out possible grain boundary effects. This makes the understanding of the physics of Ce a bit cumbersome. Despite this difficulty, we are able to track the Ce $4f$ magnetic behavior in this compound.

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