PHYSICAL REVIEW B VOLUME 39, NUMBER 4 1 FEBRUARY 1989

Magnetic susceptibility and low-temperature heat capacity of $CePd_3B_{0.3}$

S. K. Dhar* and K. A. Gschneidner, Jr.
Ames Laboratory and Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011

C. D. Bredl and F. Steglich
Institut für Festkörperphysik, Technische Hochschule Darmstadt, 6100 Darmstadt, West Germany
(Received 25 July 1988)

The heat capacity of $CePd_3B_{0.3}$ has been measured between 80 mK and 2.5 K in zero and applied fields up to 4 T. The specific heat exhibits a Schottky-like anomaly, nearly symmetric on a $\ln T$ scale, which is shifted to higher temperatures in applied fields. High-temperature susceptibility measurements confirm a near trivalent state of Ce in $CePd_3B_{0.3}$ while the ac susceptibility in the range 0.15 to 0.7 K displays a cusp at 0.45 K which is smeared out in applied fields indicating a spin-glass transition. Kondo interactions are also operative as evidenced by the large value of C/T as $T \rightarrow 0$.

I. INTRODUCTION

The heat capacity of alloys $CePd_3B_x$, $0 < x \leq 1$, has been reported by several groups in the literature.[1–4] Following the observation of a valence change of cerium ions from intermediate valent in $CePd_3$ to trivalent in $CePd_3B_x$ for $x \geq 0.25$[5], Kuentzler *et al.*[1] carried out the first heat-capacity measurements on these alloys between 1.8 and 20 K. It was found that for $x \geq 0.25$ the heat capacity C showed an upturn below 5 K, attaining values of ~ 2 J/mol K at the lowest temperature. Due to the limited low-temperature range of these measurements, the nature of the upturn could not be resolved. In a later work by Kappler *et al.*,[2] and a more extended version of it,[3] the heat capacity was measured down to 0.4 K and peaks in the heat capacity were observed at temperatures below 1.8 K, the peak temperature T_{max} varying with boron concentration x. Considerations based on the Kondo-impurity model were unable to explain the observed anomalous behavior, and these authors tentatively proposed a spin-glass state or a dense-Kondo state of a heavy-Fermi-liquid system with magnetic correlations as the likely cause of the low-temperature anomalies in $CePd_3B_x$ alloys. The former view may have been encouraged partly by the appearance of irreversible phenomena and thermal-history effects in the susceptibility of these alloys for $T < 1$ K. For $T < T_{max}$, the transitional heat capacity, after subtracting the usual lattice and electronic contributions, was found to obey a linear temperature dependence,[3] but did not extrapolate to zero when $T \rightarrow 0$. The values of the coefficient of the linear term in the temperature dependence of the heat capacity varied from 1.7 J/mol K^2 in $CePd_3B_{0.35}$ to 3.7 J/mol K^2 in $CePd_3B$, and this prompted Sereni *et al.* to claim $CePd_3B$ as the heaviest Fermi liquid to exist in metallic systems.[3]

II. EXPERIMENTAL DETAILS

In the present work, we have measured the heat capacity of $CePd_3B_{0.3}$ down to 80 mK in zero and applied fields up to 4 T. ac susceptibility was measured between 0.15 and 0.7 K in zero and applied fields of 0.1 and 1 T, respectively. dc magnetic susceptibility from 300 to 1.6 K was also studied in an external field of 0.6 T using the Faraday method. The composition of $CePd_3B_{0.3}$ was chosen because the results of Ref. 1 showed that the electronic specific-heat constant, as determined from high-temperature data in the range 9–18 K, passed through a maximum for this composition. The sample used in the present work is the same on which high-field heat-capacity results were obtained in Ref. 4.

The heat-capacity measurements of the present work employed a modified quasiadiabatic pulse method[6] in the persistent field of a superconducting solenoid. The field dependence of the thermometer, a Matsushita ERC-18 carbon resistor attached to the sample, has been accounted for. The temperature rise ΔT used to determine $C = \Delta Q / \Delta T$ was obtained from an extrapolation of the temperature readings $T(t)$ before and after the heat input ΔQ to the middle of the heating period.

III. RESULTS AND DISCUSSION

Figure 1 depicts the inverse magnetic susceptibility of $CePd_3B_{0.3}$ as a function of temperature. A Curie-Weiss behavior is observed down to 40 K with a slight deviation at lower temperatures. An effective moment of 2.56 μ_B and a paramagnetic Weiss temperature Θ_p of -6 K is obtained from the χ^{-1} versus T plot. These results are in conformity with those reported earlier in literature[5] and show that cerium ions in $CePd_3B_{0.3}$ are essentially trivalent. The low value of θ_p is generally characteristic of materials with low Kondo temperature and may have similar connotations for $CePd_3B_{0.3}$. The inset of Fig. 1 shows the results of low-temperature ac susceptibility measurements. A peak in the zero-field susceptibility occurs at 0.45 K. The application of an external magnetic field suppresses this peak, and it is totally smeared out in an applied magnetic field of 1 T. The ac susceptibility response strongly suggests that $CePd_3B_{0.3}$ undergoes a

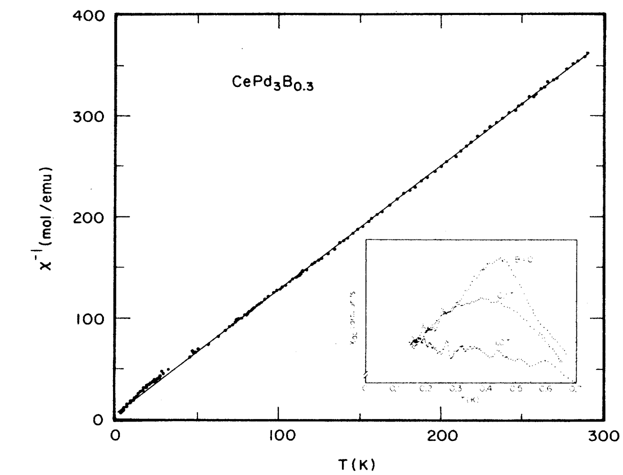

FIG. 1. The inverse molar susceptibility vs temperature of $CePd_3B_{0.3}$ in an external field of 0.6 T. The inset shows ac susceptibility (117 Hz) from 0.15 to 0.7 K in zero and applied fields of 0.1 and 1 T.

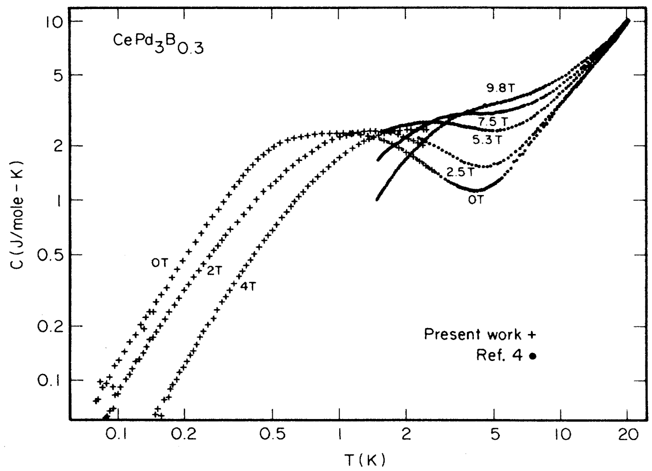

FIG. 3. The combined heat-capacity results of the present work and Ref. 4 shown on a ln-ln plot. Not all of the experimental data points are shown for the sake of clarity.

spin-glass transition below 1 K, with a freezing temperature of ~0.45 K.

The heat-capacity results are shown in Fig. 2 in the form of a C versus $\ln_{10}T$ plot. In Fig. 3, the combined data of the present work and Ref. 4 are depicted on a ln-ln plot. Heat capacity in zero field exhibits a peak at $T_{max} \sim 0.95$ K with $C_{max} = 2.36$ J/mol K. The application of an external field increases T_{max}. Qualitatively, our heat-capacity results are in accord with those reported in Ref. 3. The entropy associated with the anomaly is 5.4 J/mol K (up to 4 K), which is close to R ln2, and indicates that a doublet ground state is involved in the specific-heat anomaly. It may be noted that the specific-heat data do not show any anomaly at the temperature of the maximum in the ac susceptibility. Phenomenologically, these observations bear close resemblance to those

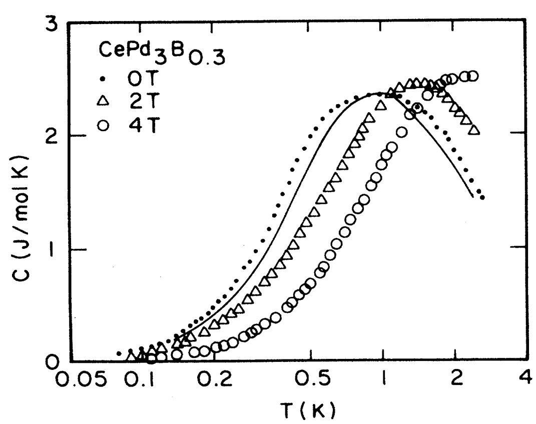

FIG. 2. The heat capacity C of $CePd_3B_{0.3}$ vs ln in fields of 0, 2, and 4 T. The solid curve depicts the results of the resonance-level model (Ref. 9), with $E/k_B = 2$ K and $\Delta/k_B = 0.9$ K.

reported on $CeCu_{6.5}Al_{6.5}$.[7] In the latter compound, a pronounced specific-heat anomaly at $T_{max} = 0.85$ K, with $C_{max} = 3.3$ J/mol K, is observed in applied fields. The anomaly is nearly symmetric on a $\ln T$ scale and shifts to higher temperatures in applied fields. Zero-field, low-frequency ac susceptibility of $CeCu_{6.5}Al_{6.5}$ shows a peak at 0.3 K which is wiped out in an external field of 0.04 T. A concentrated spin-glass state was proposed for $CeCu_{6.5}Al_{6.5}$.[7]

The peak in the ac susceptibility of $CePd_3B_{0.3}$ could also arise due to an antiferromagnetic transition, but the absence of a λ-type peak of an antiferromagnetic transition in the heat capacity rules out such a possibility. Besides, the external magnetic field would tend to lower T_{max} of the heat capacity if it were due to antiferromagnetic interactions between cerium ions, contrary to what is observed. In conjunction with ac susceptibility results, it appears that in $CePd_3B_{0.3}$ we are dealing with a spin-glass system in which the Ruderman-Kittel-Kasuya-Yosida (RKKY) coupled cerium spins freeze randomly at low temperatures. However, the system does not exhibit a linear temperature variation of the heat capacity below the maximum as found in both metallic and insulating spin glasses.[8] Although the cerium ions are occupying regular (periodic) sites in the lattice of $CePd_3B_{0.3}$, a spin-glass ground state would imply random Ce-Ce exchange interactions. It is possible that the random distribution of boron atoms in the unit cell makes the system inhomogeneous, which varies the electronic environment around cerium ions and the RKKY mediated exchange interactions between them according to the boron occupation in the near-neighborhood environment of cerium ions. A similar conclusion was drawn[7] from the results on $CeCu_{6.5}Al_{6.5}$.

The heat-capacity plots of Fig. 2, which look like broadened Schottky anomalies on a linear T scale, can be derived phenomenologically using the resonance-level model[9] in which the Zeeman separation E between two broadened levels has a Lorentzian distribution characterized by a width Δ. While T_{max} is determined by E only, the value of Δ for a given E determines C_{max}. The resonance-level model has been successfully employed to explain the specific heat of $La_{1-x}Ce_xAl_2$ alloys[10] in applied fields where the Kondo interaction between the crystal-field-split doublet ground state of the cerium ions with the conduction band broadens the Γ_7 doublet. For $CePd_3B_{0.3}$, we find $E/k_B = 2$ K and $\Delta/k_B \sim 0.9$ K come closest to representing the zero-field heat-capacity data as shown by the solid curve of Fig. 2. Our results strongly suggest that $CePd_3B_{0.3}$ is in a spin-glass state at low temperatures. We also find that the values of the coefficient of the linear term in the temperature dependence of the heat capacity reported in Ref. 3 are grossly overestimated. The randomly varying internal field of a spin-glass state is the likely cause of both the Zeeman splitting E and the width Δ in $CePd_3B_{0.3}$. However, the Kondo interaction between cerium ions and the conduction electrons may partially contribute to Δ. A fit of the zero-field data in Ref. 4 in the range 7–20 K gives an intercept of 245 mJ/mol K^2 on the C/T axis, implying appreciable Kondo interactions of cerium ions with the conduction electrons. While the Kondo interaction normally weakens the moment as one approaches the Kondo temperature and eventually leads to a singlet ground state, the appearance of the spin-glass state in $CePd_3B_{0.3}$ shows that the RKKY interaction manages to stabilize the cerium moment, which presumably is of a reduced size. This agrees with our conclusion that the Kondo interaction survives largely in the spin-glass phase as the C/T $(T \to 0)$ value is still large (see the following). The interplay of various competing interactions in $CePd_3B_{0.3}$ makes it a complex system, and our use of the resonance-level model is certainly an oversimplification. Thus, for example, the above-mentioned values of E and Δ give a $C/T\,(T \to 0)$ of 1.6 J/mol K^2 which is not in accord with the experiment as discussed above and in the next paragraph.

An examination of Fig. 4 shows that C/T in zero field attains a large value of ~ 4 J/mol K^2 at ~ 0.4 K and then decreases monotonically to ~ 1 J/mol K^2 at 80 mK, the lowest-temperature data point in the present work. Data at still lower temperatures are required to extrapolate the C/T versus T^2 plot correctly to the $T = 0$ limit to obtain the value of the linear coefficient of heat capacity γ. A reasonable value of γ can be obtained by a linear extrapolation of the lowest data points to $T = 0$ K from the C/T versus T plot shown in the inset of Fig. 4. This extrapolation gives a C/T value of ~ 150 mJ/mol K^2 as $T \to 0$, in fair (order of magnitude) agreement with the high-temperature extrapolated estimate. In Ref. 3, specific heat was measured down to 0.4 K only, and as a result, erroneously large values of γ were concluded.

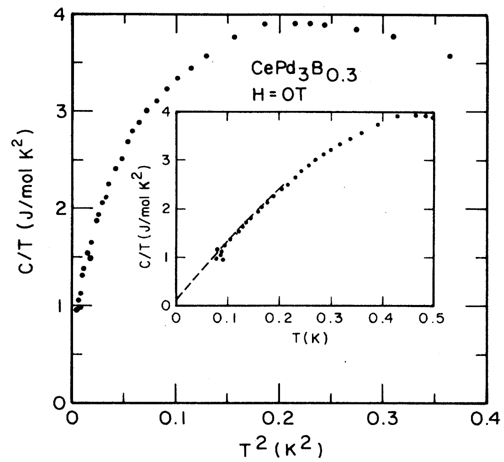

FIG. 4. The zero-field heat capacity of $CePd_3B_{0.3}$ in the form of C/T vs T^2 below 0.6 K. The inset shows C/T vs T and the dashed line is the linear extrapolation of the data below ~ 0.3 K.

In summary, $CePd_3B_{0.3}$ constitutes a second example of a periodic lattice of local Ce-derived magnetic moments that exhibit spin-glass-like properties. This rare behavior in the present case very likely reflects boron-induced disorder in the RKKY-type coupling between the Ce ions. In addition to the previously described[7] related material $CeCu_{6.5}Al_{6.5}$, substantial renormalization effects of conduction electron states due to Kondo interaction are resolved in the low-temperature heat capacity of $CePd_3B_{0.3}$.

ACKNOWLEDGMENTS

Part of the work done at Darmstadt was supported by the Sonderforschungsbereich, 252 Darmstadt /Frankfurt/Mainz/Stuttgart. The Ames Laboratory is operated for the U.S. Department of Energy (DOE) by Iowa State University under Contract No. W-7405-ENG-82. This research was supported by the Office of Basic Energy Sciences of the U.S. DOE.

*Permanent address: Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India.

[1] R. Kuentzler, S. K. Dhar, S. K. Malik, R. Vijayaraghavan, and B. Coqblin, Solid State Commun. **50**, 145 (1984).

[2] J. P. Kappler, M. J. Besnus, E. Beaurepaire, A. Meyer, J. Sereni, and G. Nieva, J. Magn. Magn. Mater. **47–48**, 111 (1985).

[3] J. Sereni, G. Nieva, J. P. Kappler, M. J. Besnus, and A. Meyer, J. Phys. F **16**, 435 (1986).

[4] S. K. Dhar, K. A. Gschneidner, Jr., O. D. McMasters, and J. F. Nakahara, J. Less-Common Met. **127**, 379 (1987).

[5] S. K. Dhar, S. K. Malik, and R. Vijayaraghavan, Phys. Rev. B **24**, 6182 (1981).

[6] Further details may be found in the Ph.D. thesis of C. D. Bredl, Technische Hochschule, Darmstadt, 1985 (unpublished).

[7] U. Rauchschwalbe, U. Gottwick, U. Ahlheim, H. M. Mayer, and F. Steglich, J. Less-Common. Met. **111**, 265 (1985).

[8] D. Meschede, F. Steglich, W. Felsch, H. Maletta, and W. Zinn, Phys. Rev. Lett. **44**, 102 (1980).

[9] K. D. Schotte and U. Schotte, Phys. Lett. **55A**, 38 (1975).

[10] C. D. Bredl, F. Steglich, and K. D. Schotte, Z. Phys. B **29**, 327 (1978).