Ground state properties of CeNi$_{12}$B$_6$

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Abstract. We report on the ground state features of the orthorhombic ternary compound CeNi$_{12}$B$_6$ which exhibits a large Ce-Ce interatomic distance of 6.07 Å. Magnetic and electronic properties were studied by means of low temperature heat capacity and electrical resistivity measurements performed down to 0.4 K, high pressure resistivity studies and by magnetic susceptibility measurements. The low temperature heat capacity reveals a sharp second order type antiferromagnetic phase transition at $T_N = 1.85$ K with an entropy gain of only $0.3 R \ln 2$ at $T_N$. The initial temperature dependence of the heat capacity as well as resistivity data is well accounted for by a model for gapped antiferromagnetic magnons yielding an exceptionally large spin wave excitation gap $\Delta \sim 2.2 T_N$. Single crystal magnetic susceptibility studies reveal a huge uni-axial single-ion crystal field anisotropy confining the moments along the orthorhombic $c$-axis. The application of quasi-hydrostatic pressure up to 1.4 GPa causes an increase of the Néel temperature to 2.3 K at 1.4 GPa.

1. Introduction

Cerium based intermetallic compounds are of special interest with respect to their variety of ground states resulting from the competition between interactions favoring the formation of symmetry breaking long range magnetic order driven by RKKY-type Ce-Ce intersite correlations versus interactions such as Kondo screening or frustration effects favoring a symmetry conserving ground state such as the paramagnetic Kondo lattice state [1]. The relevance of RKKY-type exchange coupling is generally expected to be lower in systems with large Ce-Ce interatomic distances. Accordingly, there are examples with large distances among Ce-ions, such as CeNi$_9$Si$_4$ with $d_{\text{Ce-Ce}} \sim 5.6$Å showing many features as predicted by single parameter Kondo models (with energy scale $T_K$) [2], similarly, solid solutions CeNi$_9$Ge$_{4-x}$Si$_x$ with an interplay between crystal field splitting and Kondo effect [3], or CeNi$_9$Ge$_4$ showing features of quantum criticality with a rather low Kondo energy scale [4, 5]. Of course, there are also some exceptions among Ce-systems with large Ce-Ce distance showing unexpectedly high magnetic ordering temperatures such as CeT$_2$Al$_{12}$ ($T = \text{Ru and Os}$) with $d_{\text{Ce-Ce}} \sim 5.2$Å and $T_N \sim 28$ K [6, 7, 8].

In the present paper we present first results on the ground state properties of the ternary compound CeNi$_{12}$B$_6$ which exhibits a Ce-Ce interatomic distance of 6.07 Å. An initial structural characterization was reported earlier [10, 11] and revealed a new orthorhombic structure type, space group $C'mc2_1$ according to which Ce is located in the center of a polyhedron formed by 18 nickel and 6 boron atoms. A very interesting feature of the CeNi$_{12}$B$_6$ structure displayed in Fig. 1 is the existence of slightly puckered $3^34^2$ Ni-nets ($d_{\text{Ni-Ni}} = 2.45$ Å – 2.62 Å) oriented in the $ab$-plane. Such $d$-metal sheets may give rise to highly anisotropic features of the Fermi
Figure 1. View of the CeNi$_{12}$B$_6$ structure, space group $Cmc_2_1$, with emphasis on Ni-Ni bonds. The orthorhombic unit cell is indicated by black lines.

surface and of the related electronic properties. The remaining nickel atoms are inter-bounded to form pairs of empty [Ni$_4$] tetrahedra coupled by common edges ($d_{Ni-Ni} = 2.50\ \text{Å} - 2.60\ \text{Å}$) which are highlighted in green color in Fig. 1.

2. Experimental details
Polycrystalline samples were prepared from high purity elements (4N for Ce from Ames [9], 5N for Ni, and 6N for $^{11}$B isotope with an isotope purity of 99.97%) via repeated inductive melting and subsequent annealing for one week at 1030°C. Polycrystalline LaNi$_{12}$B$_6$ was prepared as a Pauli paramagnetic reference with 4$f^0$ configuration. A large single crystal of CeNi$_{12}$B$_6$ was grown from a stoichiometric polycrystalline feed rod via the floating zone technique in a mirror furnace and was finally oriented by means of the Laue method. The quality of the CeNi$_{12}$B$_6$ crystal is indicated by a reasonably high residual resistivity ratio, $RRR \sim 30$.

X-ray powder diffraction patterns, collected by a Guinier-Huber image plate system with monochromatic Cu K$_1$ radiation ($8^\circ < 2\Theta < 100^\circ$), revealed single-phase materials. Applying the structural model reported earlier [10, 11] with space group $Cmc_2_1$, we refined the lattice constants of CeNi$_{12}$B$_6$: $a = 0.95897\ (3)\ \text{nm}$, $b = 0.74067\ (2)\ \text{nm}$, $c = 1.10681\ (3)\ \text{nm}$. Rietveld refinements of X-ray powder diffraction data converged to reliability factors as small as $R_F = 0.029$ and $R_I = 0.039$.

Heat capacity measurements in the temperature range 3 K – 125 K were carried out with a home-made adiabatic calorimeter and measurements from 0.4 K to 5 K with a Quantum Design PPMS relaxation calorimeter with $^3$He-insert. Magnetic measurements were performed on a 6 T CRYOGENIC SQUID magnetometer. The temperature dependence of the electrical resistivity was studied employing a four probe AC method on a single crystal with spot welded gold contacts using a $^3$He cryostat in the temperature range 0.5 K – 300 K. High pressure resistivity measurements up to 1.4 GPa were performed on a polycrystalline sample the temperature range 1.5 K – 300 K with a standard piston cylinder technique using Daphne oil as pressure transmitting medium.
3. Results and discussion

The low temperature heat capacity, $C(T)$, as well as the temperature dependent electrical resistivity, $\rho(T)$, of CeNi$_{12}$B$_6$ (displayed in Fig. 2) reveal a rather sharp second order type antiferromagnetic phase transition at $T_N = 1.85$ K. In both cases, for $C(T)$ and $\rho(T)$, the temperature dependencies are well in line with the model for gapped antiferromagnetic magnons with spin-wave dispersion, $\omega = \sqrt{\Delta^2 + D^2k^2}$, proposed by Continentino et al. [12], where $\Delta$ is the spin-wave gap, which arises from anisotropy with respect to magnetic interactions and/or from single ion anisotropy. $D$ is the spin-wave velocity. This ansatz yields the following analytical expressions for the electrical resistivity and specific heat,

$$\rho_{mag}(T) = A\Delta^{3/2}T^{1/2}e^{-\Delta/T}[1 + (20/30)(T/\Delta) + (2/15)(T/\Delta)^2]$$  \hspace{1cm} (1)

$$C_{mag}(T) = B\Delta^{7/2}T^{1/2}e^{-\Delta/T}[1 + (39/20)(T/\Delta) + (51/32)(T/\Delta)^2]$$  \hspace{1cm} (2)

with prefactors $A$ and $B$ being related to the spin-wave velocity $D$ by, $A \propto B \propto 1/D^3$. Least squares fits of equations (1) and (2) to the experimental data of Fig. 2 reveals convincing agreements for a spin wave excitation gap $\Delta \sim 4.1$ K $\sim 2.2T_N$ with prefactors $A = 2.29 \mu\Omega cm/K^2$ and $B = 0.184 J/(mol K^5)$. Further included in these fits are a residual resistivity term $\rho_0 = 4.4 \mu\Omega cm$ and an electronic specific heat contribution $C_{el} = \gamma T$ with $\gamma \sim 60$ mJ/(mol K$^2$).

The temperature dependent magnetic specific heat contribution, $C_{mag}(T)$, of CeNi$_{12}$B$_6$ obtained by subtracting the specific heat of LaNi$_{12}$B$_6$ (not shown) as a reference for electronic and lattice contributions is displayed in Fig. 3a together with the corresponding magnetic entropy gain $S_{mag}(T)$ in Fig. 3b. The latter reveals an entropy gain of only $S_{mag}(T_N) \sim 0.3R\ln 2$ at the magnetic transition and, thus, a significant entropy transfer towards the paramagnetic regime.
The magnetic specific heat contribution, $C_{\text{mag}}(T)$, of CeNi$_{12}$B$_6$ obtained by subtracting LaNi$_{12}$B$_6$ data as a reference for electron and phonon contributions in panel (a); corresponding magnetic entropy gain, $S_{\text{mag}}(T)$, in panel (b).

which relates to short range correlations and/or to Kondo interactions (with $T_K$ being limited to a few Kelvin). It is important to note, that the specific heat of the paramagnetic state right above $T_N$, $C(2\,K) \approx 4\, J/(\text{mol K})$, largely exceeds the theoretical maximum of the Kondo specific heat contribution, $C_{Kondo,J=1/2} \leq 1.55\, J/(\text{mol K})$, calculated for a Kondo model with a doublet ground state [13] and its origin is, thus, assigned to primarily magnetic Ce intersite short range correlations rather than to Kondo correlations.

The full entropy of the Ce-4$f^1$ crystal field (CF) ground state doublet, $S = R \ln 2$, is reached at 15 K, i.e. at $8 \times T_N$. The magnetic specific heat contribution reveals a Schottky maximum at about 55 K which places a CF doublet at $\Delta_1 \approx 120\, K$. The second doublet at $\Delta_2$ above the CF ground state doublet is expected at or above room temperature.

The temperature dependent magnetic susceptibility, $\chi(T) \equiv M/H(T)$, of single crystalline CeNi$_{12}$B$_6$ measured in a field of 3 T oriented along principle directions as labelled.
Temperature and pressure dependent electrical resistivity, $\rho(T)$, of polycrystalline CeNi$_{12}$B$_6$.

An exceptionally large uniaxial CF anisotropy is further revealed by single crystal magnetization studies displayed in Fig. 4. The easy axis of the single ion anisotropy is the crystallographic $c$-axis, while moments measured with $H||a$- and $H||b$-axis are essentially quenched at low temperatures. An almost isotropic Curie-Weiss type paramagnetic susceptibility with an effective moment near 2.54 $\mu_B$/f.u. (Ce$^{3+}$ free ion value) is restored above room temperature, thus, in line with the evolution of the magnetic entropy $S_{mag}(T)$ in Fig. 3b.

High pressure electrical resistivity data of a polycrystalline sample presented in Fig. 5 reveal a moderate increase of $T_N$ which is evaluated from first derivative of the resistivity, $d\rho/dT$, where a distinct jump in the slope of $\rho(T)$ is observed at $T_N$. Thereby, a change of the Néel temperature from 1.85 K at ambient pressure to 2.3 K at 1.4 GPa as well as an enhancement of the Kondo-like feature above $T_N$ is observed. The latter feature may also originate from magnetic short range correlations caused by dimensional frustration in addition to Kondo correlations. At temperatures below $T_N$, i.e. from 1.5 K to 1.85 K hardly any pressure induced changes of the resistivity $\rho(T)$ are observed.

The limited relevance of Kondo correlations is indicated by the positive pressure dependence of $T_N$ which places CeNi$_{12}$B$_6$ to the magnetically ordered part of the Doniach phase diagram where RKKY coupling clearly outperforms Kondo correlations (see e.g. Ref. [14]). At closer balance of RKKY and Kondo correlations in antiferromagnetic cerium Kondo lattice systems long range magnetic order is usually suppressed in favor of a paramagnetic Kondo Fermi-liquid ground state. Prominent examples are CePd$_2$Si$_2$ and CeIn$_3$ where the ambient pressure antiferromagnetic state with $T_N \sim 10$ K is suppressed at $\sim 2.4–2.8$ GPa and an unconventional superconducting phase appears [15].

Very similar features as in the present case of CeNi$_{12}$B$_6$ have been reported for another orthorhombic Ce-lattice system with similarly significant single ion anisotropy, namely, CeZn$_2$ where an initial increase of $T_N$ is reported for applied pressure up to about 1.5 GPa [16].
4. Summary and outlook
Phase pure poly- as well as single crystalline samples of CeNi$_{12}$B$_6$ were prepared by means of induction melting and zone melting, respectively. Low temperature studies of CeNi$_{12}$B$_6$ by means of heat capacity and electrical resistivity studies reveal a rather sharp magnetic phase transition at 1.85 K. The analysis of the initial temperature dependence (starting from 0.4 K) of the specific heat capacity as well as electrical resistivity data reveals a rather close agreement with a model for gapped antiferromagnetic magnons which indicates an antiferromagnetic ground state with an exceptionally large spin wave excitation gap $\Delta \sim 2.2 \, T_N$. The entropy gain at $T_N$ reaches only $0.3R \ln 2$ and, accordingly, a significant amount of entropy is transferred towards the paramagnetic regime. These features relate to a huge single ion anisotropy revealed by single crystal susceptibility studies and possibly highly anisotropic electronic features arising from nickel sheets oriented parallel to the $ab$-plane.

In order to further clarify the specific role of Kondo correlations and possibly dimensional frustration, additional low temperature studies of single crystal anisotropic properties are in progress as well as ab initio electronic structure studies.

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