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Crystal field in RPdIn (R = Ce, Pr, Nd) compounds

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ABSTRACT

The RPdIn compounds (R = rare earth) crystallise in the hexagonal ZrNiAl-type crystal structure. The compounds from this family exhibit a great variety of interesting magnetic properties including heavy fermion behaviour. In order to get a deeper insight into nature of magnetism of RPdIn with light rare earths elements (La–Nd) an inelastic neutron scattering experiment was performed. For compounds with Pr and Nd excitations due to crystal field were clearly distinguished. On the other hand, interesting behaviour for the CePdIn sample was observed. The sample exhibits no signs of crystal field excitations, likely due to highly delocalised Ce 4f states leading to its heavy fermion behaviour.

1. Introduction

Among the 1:1:1 rare-earth intermetallics the ZrNiAl-type of crystal structure was observed for many compounds [1]. Compounds crystallising in the hexagonal ZrNiAl-type structure ($P\bar{6}2m$ space group) exhibit interesting and unusual magnetic properties due to their structural properties. The structure is layered, where layers consisting of rare-earth and d-electron metal are separated by non-magnetic layers of d-electron metal and p-electron elements. The rare earth sites exhibit orthorhombic symmetry forming a distorted kagomé lattice [2].

Magnetic properties of the RPdIn family were reported in number of works. The CePdIn compound was the subject of the most extensive studies. The sample exhibits heavy fermion behaviour with the Sommerfeld coefficient of electronic specific heat above 500 mJ/mole K^2, moreover the magnetic ordering was evidenced as well, with the ordering temperature of about 1.6 K [3,4]. The PrPdIn sample does not exhibit signs of magnetic ordering down to 1.7 K [5], whereas NdPdIn orders ferromagnetically at about 30 K [5,6]. For RPdIn samples with heavy rare earths magnetic ordering was observed for R = Gd (102 K); R = Tb (70 K); R = Dy (34 K); R = Ho (25 K) and R = Er (12.3 K) [7].

Crystal field effects of RPdIn compounds were studied only by means of specific heat for CePdIn, PrPdIn and NdPdIn [5]. For all RTX alloys crystallising within the ZrNiAl-type crystal structure there are just few approaches to determine crystal electric field (CEF) levels schemes, by means of specific heat and inelastic neutron scattering (INS), mainly for the RNiAl family [8–12].

2. Experimental details

Polycrystalline samples of RPdIn (R = La–Nd) were prepared by arc melting of the constituents (R: 99.9 wt%; Pd: 99.99 wt%; In: 99.99 wt%) under a titanium-gettered argon atmosphere. The resulting ingots were re-melted several times in order to ensure homogeneity. Then, annealing in an evacuated silica tube at 870 K for 100 h was applied.

The quality of the sample was checked by X-ray powder diffraction at room temperature using a Siemens D5000 diffractometer (Cu Kα radiation). All samples exhibited the desired ZrNiAl-type crystal structure without impurity phases.

Inelastic neutron scattering experiments were performed at the V3 (NEAT) time of flight spectrometer at the BERII research reactor in BENSC Berlin. The incident neutrons energy was 10.6 meV. For the CePdIn sample additional measurements were performed with neutrons of energy equal to 18.4 meV. The LaPdIn sample was measured as a non-magnetic analogue in order to estimate the

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phononic contribution. The relative efficiencies of the detectors banks were calibrated using a standard vanadium sample.

3. Results

Within the ZrNiAl-type of crystal structure the rare earth ions are located at special positions of orthorhombic point symmetry C_{2v}. Thus, despite the formal hexagonal symmetry the crystal field hamiltonian with nine parameters must be taken into account:

$$H_{CEF} = B_2^0\hat{O}_2^0 + B_2^2\hat{O}_2^2 + B_4^0\hat{O}_4^0 + B_4^2\hat{O}_4^2 + B_4^4\hat{O}_4^4 + B_6^0\hat{O}_6^0 + B_6^2\hat{O}_6^2 + B_6^4\hat{O}_6^4 + B_6^6\hat{O}_6^6 \quad (1)$$

where the B_n^m are crystal field parameters and O_n^m are the Stevens operators. It is obvious, that such a large number of parameters will make any analysis of crystal field in the light of experimental data ambiguous. This has been proved recently in the case of inelastic neutron scattering for an isostructural ErNiAl compound [10]. It turned out, that there are several sets of CEF parameters, which reproduce the experimental data properly. Such a low symmetry leads to lifting of the ground multiplet into doublets or singlets for Krammers (even J number) and non-Krammers (odd J number) ions, respectively. In case of Ce and Nd-based compounds 3 and 5 doublets are expected, respectively. For Pr-based ones 9 singlets are present.

3.1. CePdIn

An inelastic neutron scattering experiment performed for the CePdIn sample did not revealed a noticeable contribution from the crystal electric field (CF) at energies up to 18.4 meV in the gain energy regime. Accordingly no contribution originating from depopulating of the excited CF levels was observed in the loss energy regime up to 300 K. In Fig. 1 experimental data collected for incident neutrons of energy of 10.6 meV at 2 and 300 K are presented. According to specific heat estimations the first excited doublet should lie at about 6.4 meV above the ground CF state. At this energy no anomaly was evidenced. An asymmetry at the gain side of the elastic line, visible in the Fig. 1, is connected to the phononic excitations. The observed behaviour is likely connected with highly delocalised 4f states of Ce ions resulting from hybridisation with the conduction band. The above conclusion is supported with the very low magnetic moment of 0.1 μ_B (within magnetically ordered state) attributed to the Ce ions, as derived in Ref. [3].

3.2. PrPdIn

INS spectra for PrPdIn sample are presented in Fig. 2. The respective transitions scheme is given in Fig. 3. At a temperature of 3 K only transitions from the ground CF level are expected. Within the investigated energy range just 4 transitions, marked by A, B, C and D, are visible. The transition from ground CF level to level located at 5.77 meV was not observed. This is connected with vanishing of the transition matrix element between these two levels. The existence of this state may be deduced from high temperature data, when it becomes thermally populated.

At a temperature of 50 K first (1.46 meV) and second (3.10 meV) excited CF levels become populated (see Figs. 2b and 3). Thus, transitions from these levels become visible (E, F). Moreover, 3 transitions at the gain energy range are visible as well (A, B, E). The first two are transitions to the ground CF level, whereas the E is between second and first excited CF level (see Fig. 3).

When rising the temperature up to 100 K some new transitions, mainly from the second excited CF level (3.10 meV), are visible (Fig. 2c). Thermal population of higher levels results with the appearance of F and G transitions from the third excited CF level (5.77 meV) to the second and first excited CF levels, respectively. The transition to the ground CF state is not visible for the reason discussed above.

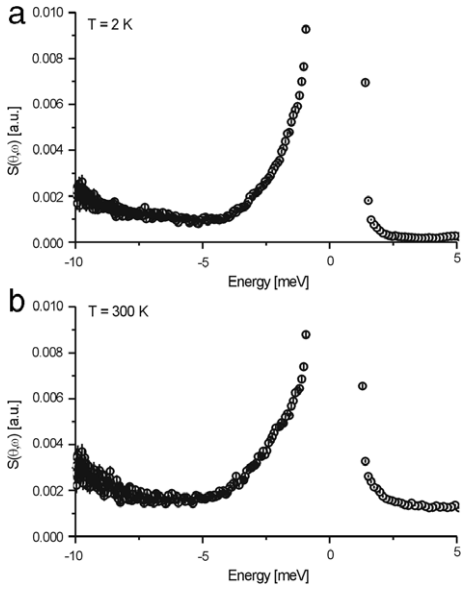

Fig. 1. Inelastic neutron scattering spectra for CePdIn sample at temperatures of 2 K (a) and 300 K (b). Experimental errors are marked by vertical lines. Incident neutron energy is 10.6 meV.

At a temperature of 200 K the last accessible 7th CF level is populated from the 6th one (transition J) as can be noticed in Fig. 2(d). For energy gain part of the spectra at least three transitions G, F, H may be visible. Closer investigation of high energy gain spectra leads to a conclusion that the weak anomaly at about 19 meV could be attributed to a transition from the 7th level directly into the ground CF level.

In the Fig. 3 CF level scheme as derived from INS is compared to that obtained on basis on Schottky contribution to the specific heat [5]. Just first 7 levels, accessible in the INS experiment, are drawn. As one can see, there is a very good agreement between CF levels schemes determined by means of both techniques.

3.3. NdPdIn

The NdPdIn sample orders magnetically roughly below 30 K. This implies that the distribution of the CF levels may vary due to presence of the molecular field. Moreover in case of Krammers ion the ground doublet becomes split. Thus, it was expected that INS spectra below the ordering temperature may exhibit some signs of influence of the molecular field. Fig. 4 shows INS spectra measured below and above the ordering point.

The Fig. 4a presents data collected at a temperature of 2 K. As one can see, at least four distinct anomalies are visible at 1.85, 4.15, 6.14 and 9.23 meV. Moreover, an additional anomaly at 0.52 meV was evidenced (the corresponding CF level scheme is given in Fig. 5). The latter anomaly originates from splitting of the ground CF doublet, whereas the former ones are connected with transitions from the ground CF level into subsequently excited levels (probably all are doublets). Just below the transitions marked by B, C and D some contribution is visible (the most intense is below the C anomaly). It is likely, that it comes either from splitting of the ground state or from splitting of the levels being excited. The overall CF splitting is higher than those estimated from specific heat studies due to presence of the molecular field.

In Fig. 4b, c data collected above the ordering temperature are shown. The distribution of CF levels is different, as transitions F