

# Magnetism and Crystal Field in PrCuAl<sub>3</sub> and NdCuAl<sub>3</sub>

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During the last five years we developed method to calculate crystal field and magnetism of rare-earth ions in solids. The method is fully *ab initio* with the exception of a single parameter which adjust the position of *f* states relative to other valence states and it was successfully applied in insulating systems. In this contribution the method is used to explain multiplet splitting and magnetism in PrCuAl<sub>3</sub> and NdCuAl<sub>3</sub> intermetallics. For the Nd compound the agreement between theory and experiment is good, while for the PrCuAl<sub>3</sub> the agreement is less satisfactory which can be due to the more delocalized 4*f* electrons of Pr<sup>3+</sup> comparing to Nd<sup>3+</sup> ion.

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## 1. Introduction

Magnetism of the rare-earth compounds is strongly influenced by the crystal field. In the transparent compounds the optical spectra may be used to determine the crystal field parameters (CFP) which are subsequently substituted in the atomic-like Hamiltonian. Its diagonalization yields the energies of crystal field split multiplets and, when the interaction with magnetic field is added, also the contribution of rare-earth (R) ions to the magnetism. The intermetallic rare-earth compounds are non-transparent so that such approach cannot be used. Theoretical estimation of CFP is thus vital for understanding the physics of these compounds.

In the past we developed a method which yields reliable values of CFP in insulators containing the R<sup>3+</sup> ions [1–5]. The method starts with the density functional theory based band structure calculation, followed by a transformation of the Bloch to Wannier basis. The local Hamiltonian is then expanded in terms of the spherical tensor operators. Resulting CFP are inserted in an atomic-like Hamiltonian involving the crystal field, 4*f* electron correlation, spin-orbit coupling, and the Zeeman interaction. The hybridization of the 4*f* states with ligand orbitals is taken into account via hybridization parameter  $\Delta$ , which is the only parameter used to improve agreement with the experiment.

The main purpose of this paper is to test the method on two intermetallic rare-earth compounds NdCuAl<sub>3</sub> and PrCuAl<sub>3</sub>. Using the neutron scattering Adroja and Anand [6] detected all levels of the crystal-field split ground multiplet of NdCuAl<sub>3</sub> and measured the field dependence of the magnetization, as well as the temperature dependence of the susceptibility. Adroja and Anand [6] made similar measurements for PrCuAl<sub>3</sub>, but in this case from the five excited levels of the ground multiplet only two were detected.

As the method was described already several times before [1–5] we do not repeat a complete description here. In the next section the details of calculation are given, followed by the results and comparison with experiment. The paper is closed by the conclusions.

## 2. Details of calculation

The results reported here were obtained using the WIEN2k [7] and wannier90 [8] packages. To calculate the multiplet splitting and magnetism modified “lanthanide” program [9], as well as our own programs were employed.

The procedure is started by the standard non-spin polarized WIEN2k calculation with the R(4*f*) states treated by an open-core method [7]. The experimental crystal structure [6] was used for both compounds. The number of *k* points in the full Brillouin zone was 1728 and the number of the basis function was  $\simeq 615$ . The exchange-correlation of the generalized-gradient approximation form [10] was used. The atomic spheres radii were 2.3, 2.1, and 1.9 a.u. for R, Cu, and Al atoms, respectively.

In the next step the R(4*f*) states are treated as the valence states to allow their hybridization with the states of other atoms. We checked that the dominating hybridization of R(4*f*) is with Cu(3*d*) states. Relative position of Cu(3*d*) and R(4*f*) states is adjusted by adding to the Cu(3*d*) potential a shift term. This term operates only on the Cu(3*d*) states and within the subspace of these states it has a simple form  $V_{shift} = \Delta \hat{I}$ , where  $\Delta$  is the hybridization parameter and  $\hat{I}$  is the  $5 \times 5$  unit matrix. Hybridization with valence states other than Cu(3*d*) is prevented by adding to the potential acting on these states a large ( $\approx 80$  eV) shift potential. Parameter  $\Delta$  was varied in broad limits  $-40 \text{ eV} < \Delta < 40 \text{ eV}$ . For NdCuAl<sub>3</sub> the Cu(3*d*) and Nd(4*f*) states are clearly separated if  $\Delta < 1.8 \text{ eV}$  and  $\Delta > 2.6 \text{ eV}$ , so that the region of Cu(3*d*) and Nd(4*f*) states overlap is  $\simeq 0.8 \text{ eV}$ . In the case of PrCuAl<sub>3</sub> the region of the overlap is broader  $2.7 \text{ eV} < \Delta < 3.8 \text{ eV}$  and close to this region the Cu(3*d*)–Pr(4*f*) hybridization still remains appreciable.

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Using the wannier90 package [8] the  $R(4f)$  Wannier functions are constructed from the Bloch eigenfunctions. The most important result for what follows is the Hamiltonian expressed in the basis of the  $4f$  Wannier functions. From this Hamiltonian the part localized on the  $R^{3+}$  ion in the unit cell located in the origin is extracted and its decomposition yields the CFP (see Refs. [1–5] for details). The local symmetry of the R site is tetragonal and, as a consequence, five real CFP  $B_0^2$ ,  $B_0^4$ ,  $B_0^6$ ,  $B_4^4$  and  $B_4^6$  are sufficient to describe the crystal field. The dependence of these parameters on  $\Delta$  is displayed in Fig. 1.

Atomic-like Hamiltonian  $\hat{H}_{at}$  on which are based the calculations described below consists of the spherically symmetrical free-ion part  $\hat{H}_{free}$ , the crystal field Hamiltonian  $\hat{H}_{cf}$  and the interaction with an external magnetic field  $\hat{H}_{Zeem}$ . The results only weakly depend on the parameters of  $\hat{H}_{free}$  and we adopted for them the values determined by Carnall et al. [11] by fitting the optical spectra of  $R^{3+}$  impurities in  $\text{LaF}_3$ .  $\hat{H}_{at}$  is diagonalized in the basis of all  $N$  single electron states originating from  $4f^n$  configuration ( $n = 2, 3$ ;  $N = 91, 364$  for  $\text{Pr}^{3+}$  and  $\text{Nd}^{3+}$ , respectively).

The magnetic moment in both compounds is strongly anisotropic. The Pr compound exhibits an Ising-like behavior, for Nd compound the anisotropy is substantial but less pronounced. The experimental results were obtained on the polycrystalline samples. We approximated the averaging of the magnetic moment in the polycrystals by taking the weighted sum for symmetry directions.

### 3. Results

As seen from Fig. 1 for  $|\Delta| \gtrsim 5$  eV the crystal field is insensitive to this parameter and the same holds then

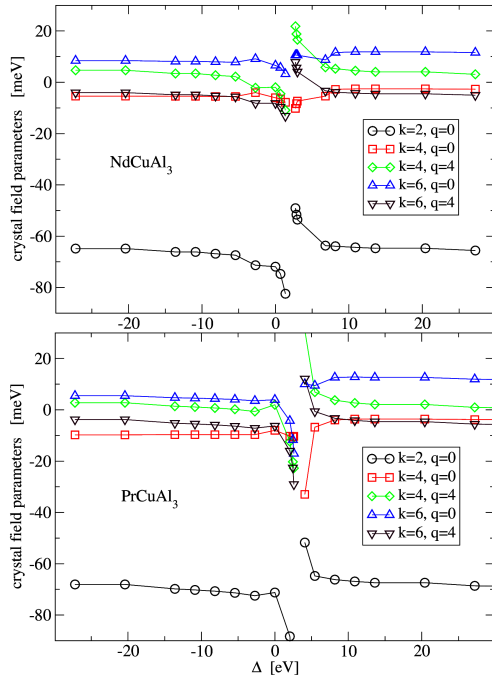


Fig. 1. Dependence of CFP on hybridization parameter.

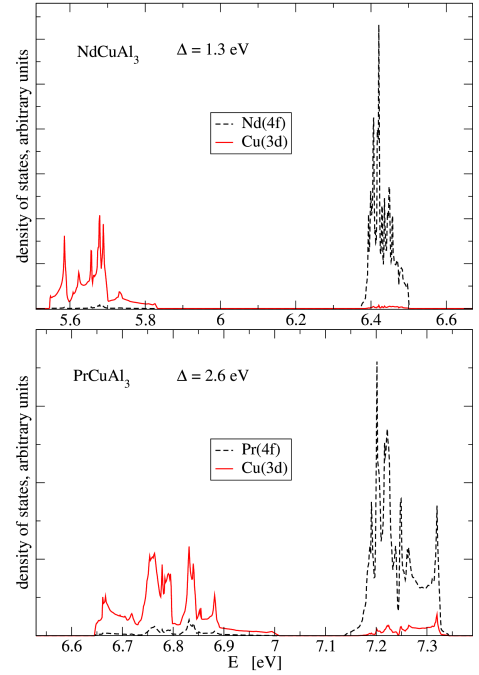


Fig. 2. Density of states projected on  $\text{Cu}(3d)$  and  $R(4f)$  states.

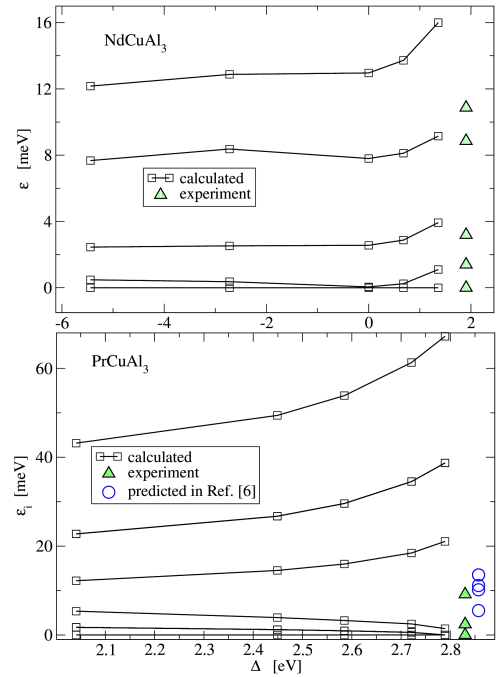


Fig. 3. Dependence of energies of ground  $R^{3+}$  multiplet on the parameter  $\Delta$ . Experimental data were taken from Ref. [6].

for the multiplet splitting and magnetism. It means that hybridization for  $|\Delta| \gtrsim 5$  eV has little effect and the properties of  $R^{3+}$  ions reflect only the electrostatic field of the crystal environment. We focus our attention on a narrow interval of  $\Delta$  for which the  $\text{Cu}(3d)$  bands lie below, but close to the  $R^{3+}$  bands, whose situation is likely to

correspond to the reality. The density of states projected on Cu(3d) and Nd(4f) states are shown in Fig. 2. The energies of the ground multiplets  $^3H_4$  of  $Pr^{3+}$  and  $^4I_{9/2}$  of  $Nd^{3+}$  split by the crystal field are displayed as functions of  $\Delta$  and compared with experiment [6] in Fig. 3.

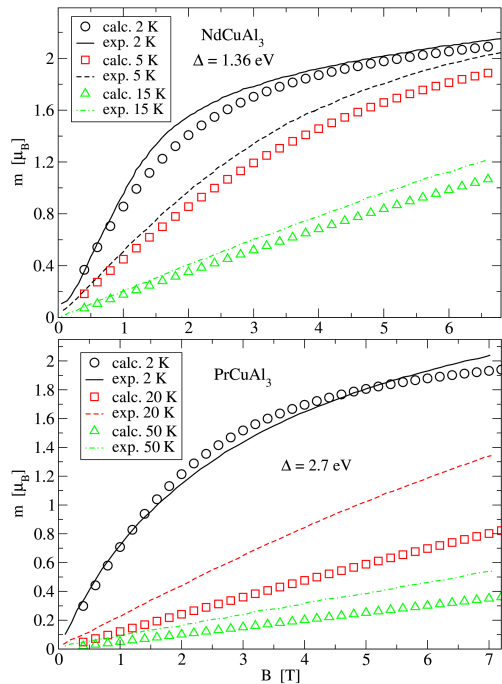


Fig. 4. Dependence of  $R^{3+}$  magnetic moment on external magnetic field. Experimental data were taken from Ref. [6].

The dependence of the magnetic moment on external magnetic field calculated at three different temperatures are compared with the experiment [6] in Fig. 4. Note that for  $Pr^{3+}$   $\Delta$  is larger than its optimal value in Fig. 3. The reason is that for  $\Delta \leq 2.6$  eV the 2 K magnetic moment is significantly reduced in disagreement with experiment.

#### 4. Conclusions

For  $PrCuAl_3$  the agreement is good for the two experimentally detected levels and for  $m(B)$  dependence measured at 2 K. For  $T = 20$  and 50 K calculated magnetic

moment is significantly smaller than experiment. This is likely to be connected with very strong sensitivity of calculated results to the gap between  $Pr^{3+}(4f)$  and  $Cu(3d)$  states in the region of small gap values. The agreement between theory and experiment for  $NdCuAl_3$  is fair for both the multiplet splitting (Fig. 3) and the magnetic moment (Fig. 4). The  $R^{3+}(4f)$ – $Cu(3d)$  hybridization is important - the calculations showed that the agreement for both quantities worsen as the gap between these states increases and hybridization becomes smaller.

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