# First principles calculation of the crystal field splitting in rare earth borocarbides *)

M. Diviš, J. Rusz

*Department of Electronic Structures, Charles University,*
*Ke Karlovu 5, 121 16 Praha 2, Czech Republic*

G. Hilscher, H. Michor, P. Blaha, K. Schwarz

*Vienna University of Technology, Karlsplatz 13, A–1040 Wien, Austria*

Received 8 October 2001

The crystal field (CF) interaction was calculated from first principles for the $RNi_2B_2C$ (R = Pr, Nd, Sm and Er) borocarbides. The parameters of the CF hamiltonian were used to obtain the CF splitting of the ground state multiplets of the $R^{3+}$ ions. This allows a comparison of the calculated specific heat of $NdNi_2B_2C$ with the experiment yielding qualitatively good agreement.

*PACS*: 71.70.Ch, 75.10.Dg
*Key words*: rare earth borocarbides, crystal field

## 1 Introduction

The quaternary intermetallic superconducting compounds $RNi_2B_2C$ (R = Sc, Y, rare earth) are ideal model systems to study the interplay between superconductivity and magnetism, when the R-ion carries a magnetic moment [1]. For a deeper understanding of magnetism in these compounds the detailed knowledge of the crystal field (CF) interaction and the related CF splitting of the localized and highly correlated 4f states is very important. As the CF interaction at the R-site is of tetragonal symmetry, it is difficult to obtain reliable starting CF parameters $A_2^0\langle r^2\rangle$, $A_4^0\langle r^4\rangle$, $A_4^4\langle r^4\rangle$, $A_6^0\langle r^6\rangle$ and $A_6^4\langle r^6\rangle$ for the interpretation of the experimental results. Gasser *et al.* [2] used modified point-charge model (MPCM) for this purpose and succeeded to obtain consistent sets of CF parameters for R = Ho, Er, and Tm which reproduce neutron spectroscopy data. In this work we propose a first principles method for the calculation of the CF parameters which is based on the density functional theory (DFT). In particular we apply this method to the light $RNi_2B_2C$, R = Nd.

## 2 Method, results and discussion

The interaction with the CF produced by the neighboring core charges and the anisotropic valence electronic charge density is the strongest perturbation of the localized atomic-like 4f states of trivalent R ions in borocarbides. In the tetragonal

---

*) Presented at 11th Czech and Slovak Conference on Magnetism, Košice, 20–23 August 2001

symmetry the corresponding CF hamiltonian can be written as

$$\hat{H}_{\mathrm{CF}} = \alpha A_2^0 \langle r^2 \rangle \hat{O}_2^0 + \beta \left( A_4^0 \langle r^4 \rangle \hat{O}_4^0 + A_4^4 \langle r^4 \rangle \hat{O}_4^4 \right) + \gamma \left( A_6^0 \langle r^6 \rangle \hat{O}_6^0 + A_6^4 \langle r^6 \rangle \hat{O}_6^4 \right), \quad (1)$$

where $\hat{O}_l^m$ are the Stevens' "operator equivalents" and $\alpha$, $\beta$ and $\gamma$ are the reduced matrix elements [3]. To calculate $A_l^m \langle r^l \rangle$ we use a first principles method based on the DFT. Within this method the electronic structure and the corresponding distribution of the ground state charge density is obtained using the full potential linearized augmented plane wave method (LAPW) implemented in the latest version of the WIEN97 code [4]. For computational details of these calculations for $\mathrm{RNi_2B_2C}$ see Diviš *et al.* [5]. The CF parameters $A_l^m \langle r^l \rangle$ originating from the aspherical part of the the total single particle DFT potential in the crystal, can be obtained from

$$A_l^m \langle r^l \rangle = a_l^m \left( \int_0^{R_{\mathrm{MT}}} |R_{4f}(r)|^2 V_l^m(r)\, r^2 dr + \int_{R_{\mathrm{MT}}}^{R_{\mathrm{c}}} |R_{4f}(r)|^2 W_l^m(r) r^2 dr \right), \quad (2)$$

where $V_l^m(r)$ and $W_l^m(r)$ are the components of the total (Coulomb and exchange-correlation) potential inside the atomic sphere with radius $R_{\mathrm{MT}}$ and in the interstitial region, respectively. The term $V_l^m(r)$ is readily obtained with the WIEN97 code. The new feature of our approach is the second term which was previously neglected since radial wave function $R_{\mathrm{4f}}$ vanish quickly for larger $r$. However, since the asphericity of the potential becomes usually large with increasing $r$, contributions from outside atomic sphere should not be neglected. The $W_l^m(r)$ is calculated using an exact transformation of the Fourier representation of the LAPW potential into a spherical Bessel function expansion between the radius $R_{\mathrm{MT}}$ and an upper radial limit $R_{\mathrm{c}}$ beyond which the 4f charge density can be neglected. The $R_{\mathrm{4f}}$ describes the radial shape of the localized 4f charge density of the $\mathrm{R}^{3+}$ ion. In the present study we used a self-interaction corrected (SIC) wave function from atomic calculations. This approach (see [6]) was found to provide a 4f charge density being very close to that obtained from more rigorous SIC-DFT band calculations [7]. The conversion factors $a_l^m$ establish the relation between the symmetrized spherical harmonics used within LAPW and the real tesseral harmonics which transform in the same way as tensor operators $O_l^m$ [6]. The following CF parameters were obtained for $\mathrm{ErNi_2B_2C}$ from equation (2): $A_2^0\langle r^2 \rangle = -90.7\,\mathrm{K}$, $A_4^0\langle r^4 \rangle = 19.6\,\mathrm{K}$, $A_4^4\langle r^4 \rangle = -140\,\mathrm{K}$, $A_6^0\langle r^6 \rangle = 6.3\,\mathrm{K}$ and $A_6^4\langle r^6 \rangle = -51\,\mathrm{K}$. The values have similar signs and magnitudes as the experimental CF parameters (see Table 2 of [2]). In the case of $\mathrm{ErNi_2B_2C}$ the CF of tetragonal symmetry splits the $J = 15/2$ state into eight doublets. Diagonalizing the CF hamiltonian (1) with the above CF parameters yields the CF level scheme (called DFT) shown in Fig.1a. This level scheme should be compared with those derived from the MPCM model [2] and from the final analysis of the inelastic neutron spectroscopy (INS) data [2], respectively. The DFT level scheme has a similar total CF splitting as the experimental one (18 meV) but differs from the MPCM spectrum. This fact suggests that our DFT CF parameters can be used as good starting values for the analysis of the INS data. Gasser *et*

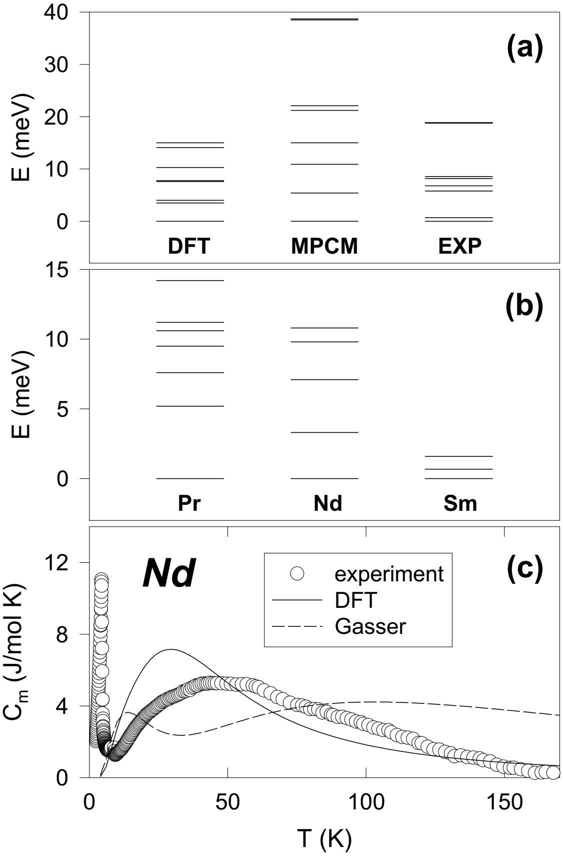

Fig. 1. The CF splitting of the ground state multiplet of Er calculated using DFT, MPCM and experimental CF parameters (a). The CF splitting of the ground state multiplets of Pr, Nd and Sm calculated using DFT CF parameters (b). The experimental 4f contribution to the specific heat of $NdNi_2B_2C$ (circles) was compared with the corresponding theoretical predictions calculated using our DFT CF parameters (full line) and calculated using extrapolated CF parameters (dashed line) from Gasser *et al.* (c).

*al.* [2] also extrapolated the experimental CF parameters of R = Tm to the light (R = Pr, Nd and Sm) borocarbides and predicted the CF splitting of the corresponding ground state multiplets (see Fig. 17 of [2]).

Shown in Fig. 1b is the CF splitting of the ground state multiplets for R = Pr, Nd and Sm calculated from our DFT approach. Comparing our CF splittings with those predicted by extrapolation [2] one can see that our total CF splittings are generally much smaller than those from Gasser et al [2]. For instance in the case of R = Nd we found a DFT-CF splitting of $J = 9/2$ multiplet of about 10 meV whereas the extrapolated CF splitting is almost 40 meV. This fact motivated us to measure specific heat. The contribution of 4f electrons to the specific heat (including magnetic and CF Shottky specific heat) was obtained by subtraction of the specific heat of $LaNi_2B_2C$ from that of $NdNi_2B_2C$ (see Fig. 1c), since the phonon contribution of both compounds can be assumed to be rather similar. We compared the experimental specific heat with that calculated using the two different (ground state) level splittings. Note, we clearly observe the sharp anomaly due to antiferromagnetic ordering at $T_\mathrm{N} = 4.8\,\mathrm{K}$ as found in neutron diffraction studies [8]. In addition we clearly resolve the Schottky type anomally centered around 50 K. The calculated Schottky contribution using our DFT-CF parameters also exhibits one maximum centered around 35 K, whereas the calculation using the extrapolated CF parameters from [2] provide two broad peaks at 20 K and 100 K with similar height. Especially the existence of the second maximum is not supported by the experiment.

In summary we calculated the CF interaction for $RNi_2B_2C$ using first principles DFT method. In the case of R = Nd we demonstrated that our approach can be used to estimate the CF parameters, CF energies and various measurable quantities, which are in fair agreement with the experiment. The work on other $RNi_2B_2C$ systems is in progress.

The work of M.D. and J.R was supported by GACR (N. 202/00/1602, N. 202/99/0184), GAUK (N. 145/2000/B) and KONTAKT 1999/21.

## References

[1] G. Hilscher and H. Michor: in *Studies on High Temperature Superconductors* (Ed. A.V. Narlikar), Nova, New York, 1999, Vol. 28, p. 242.

[2] U. Gasser, P. Allenspach, F. Fauth, W. Henggeler, J. Mesot, A. Furrer, S. Rosenkranz, P. Vorderwisch, and M. Buchgeister: Z. Phys. B **101** (1996) 345.

[3] M.T. Hutchings: Solid State Phys. **16** (1964) 227.

[4] P. Blaha, K. Schwarz, and J. Luitz: WIEN97, Vienna University of Technology, 1997.

[5] M. Diviš, K. Schwarz, P. Blaha, G. Hilscher, H. Michor, and S. Khmelevskyi: Phys. Rev. B **62** (2000) 6774.

[6] P. Novak: Phys. Status Solidi B **198** (1996) 729.

[7] M. Richter: J. Phys. D **31** (1998) 1017.

[8] J. W. Lynn, S. Skanthakumar, Q. Huang, S.K. Sinha, Z. Hossain, L.C. Gupta, R. Nagarajan, and C. Godart: Phys. Rev. B **55** (1997) 6584.