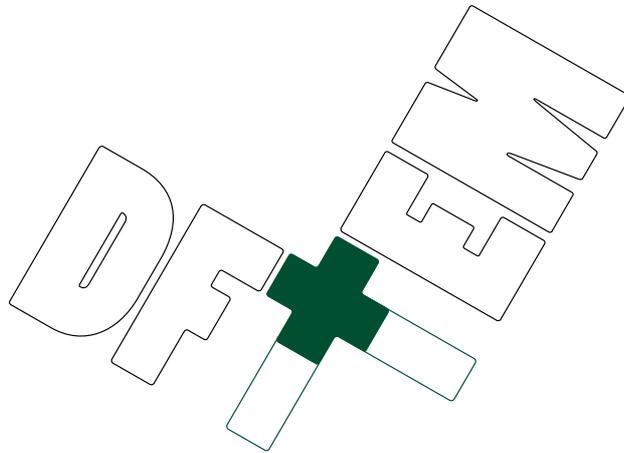


Joachim Luitz et al. (Eds.)

**DFTEM 2006 – bringing together two communities**

International Conference on  
Density Functional Theory and  
Transmission Electron Microscopy

April 21 - 23, 2006  
Vienna / Austria



Supported by Magistrat der Stadt Wien, bm:bwk and EMS

Edited by  
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Peter Blaha, Claudia Ambrosch-Draxl and Peter Schattschneider

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Proceedings of the International Conference on  
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Editio Amici – Physicae et chimicae solidorum amici  
Beatrixgasse 26/86, A-1030 Wien / AUSTRIA

Cover design ©2006 by Larissa Cerny, larissacerny.com

ISBN 3-902548-00-2 (978-3-902548-00-9)

## Magnetic properties of NdNi<sub>2</sub>B<sub>2</sub>C from first principles calculations

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The interplay between magnetism and superconductivity is inherently of great interest, since the two phenomena represent ordered states which in most systems are mutually exclusive. Therefore, the borocarbide intermetallic quaternaries with the stoichiometry RENi<sub>2</sub>B<sub>2</sub>C have attracted great attention since their discovery in 1994 [1,2], as they exhibit a coexistence of magnetism and superconductivity provided the rare earth (RE) is either Dy, Ho, Er, or Tm (see Ref. [3] and references therein). In these compounds the magnetic moments are due to the localized 4f electrons of the rare earth ions. The states of localized 4f electrons are subject to crystal field (CF) interactions and are weakly coupled to the valence electrons by the exchange interaction, resulting in the indirect Ruderman-Kittel-Kasuya-Yoshida (RKKY)-like interaction between the 4f moments.

The CF interaction in cases of RE = Dy, Ho, Er and Tm was studied by inelastic neutron spectroscopy (INS) [4]. In this paper [4] CF parameters in a microscopic CF hamiltonian were suggested. Recently the CF excitations of ErNi<sub>2</sub>B<sub>2</sub>C were measured by Raman scattering and a new level scheme was proposed for the ground state  $J = 15/2$ , whose multiplet is split by the CF interaction [5]. This new CF level scheme, however, differs from the earlier one suggested by INS [4]. Therefore a possible revision of the CF parameters proposed in [4] was suggested in [5]. From these facts the interest continues about the electronic structure of 4f states in heavy RE borocarbides.

In contrast to the heavy RE borocarbides the electronic structure and magnetic properties of the light RE borocarbides were only partially studied, in particular the NdNi<sub>2</sub>B<sub>2</sub>C case. Therefore we calculate in this paper the parameters of the microscopic CF hamiltonian from a first principles method based on density functional theory (DFT) and compare the theoretical crystal field splittings with the earlier CF parameters extrapolated from heavy RE borocarbides [6]. (see the Table, first and second row). The comparison of our new experimental specific heat and magnetic susceptibility data with the calculations is provided. The reasonable agreement between experiment and calculations is based on the new CF parameter searching method, which takes into account as a starting estimate the results of our first principles calculations.

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 RE ions in borocarbides. In the tetragonal symmetry the corresponding CF hamiltonian can be written as

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

where  $\hat{O}_l^m$  are the Stevens "operator equivalents" and  $\alpha$ ,  $\beta$  and  $\gamma$  are the reduced matrix elements [7]. 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 plus local orbitals method (APW+lo) implemented in the latest version of the WIEN2k code [8]. For computational details of these calculations for  $\text{RENi}_2\text{B}_2\text{C}$  see Diviš et al. [9]. In this work we used the local density approximation (LDA) but we checked that the results are quite similar using the generalized gradient approximation (GGA). The CF parameters  $A_l^m \langle r^l \rangle$  originating from the aspherical part of the total single particle DFT potential in the crystal, can be obtained from

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

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 (AS) with radius  $R_{MT}$  and its continuation in the interstitial region, respectively. The term  $V_l^m(r)$  is readily obtained with the WIEN2k code. The new feature of our approach is the second term, which previously was neglected, since often the radial wave function quickly decays for larger  $r$ . However, contributions from outside the atomic sphere should not be neglected, since the asphericity of the potential usually becomes large with increasing  $r$ . The term  $W_l^m(r)$  is calculated using a transformation of the Fourier representation of the APW+lo potential into a spherical Bessel function expansion between the radius  $R_{MT}$  and an upper radial limit  $R_c$  beyond which the 4f charge density can be neglected. The  $R_{4f}$  describes the radial shape of the localized 4f charge density of the RE atom. In the present study we used a self-interaction corrected (SIC) wave function from atomic calculations. This approach (see [10]) was found to provide a 4f charge density being very close to that obtained from more rigorous SIC-DFT band calculations [11]. The conversion factors  $a_l^m$  establish the relation between the symmetrized spherical harmonics used within APW+lo and the real tesseral harmonics which transform in the same way as the tensor operators [7]. In many practical cases the second order CF parameter  $A_2^0 \langle r^2 \rangle$  is the leading axial term that determines the type of magnetic anisotropy. Therefore it is interesting to obtain a deeper physical insight about the spatial origin of  $A_2^0 \langle r^2 \rangle$ . We decompose this CF parameter into the contributions originating from Coulomb on-site (inside the AS), Coulomb lattice and exchange correlation terms. The Coulomb on-site contribution can be obtained from the charge density  $\rho_2^0(r)$  using the formula

$$A_2^0 \langle r^2 \rangle_{\text{on-site}}^{\text{Coulomb}} = a_2^0 \frac{4\pi}{5} \int_0^{R_{MT}} |R_{4f}(r)|^2 r^2 \left( \frac{1}{r^3} \int_0^r \tilde{r}^4 \rho_2^0(\tilde{r}) d\tilde{r} + r^2 \int_r^{R_{MT}} \frac{\rho_2^0(\tilde{r})}{\tilde{r}} d\tilde{r} \right) dr \quad (3)$$

Now we calculate the total Coulomb contribution using eq. 2, where we replace  $V_l^m(r)$  and  $W_l^m(r)$  by the corresponding Coulomb potential components, and subtract the Coulomb on-site contribution, which gives the Coulomb lattice contribution. The exchange correlation contribution can be obtained by subtracting the total Coulomb contribution from the final value of the  $A_2^0 \langle r^2 \rangle$  CF parameter. Now we follow the decomposition of the electric field gradient into orbital contributions, namely the p-p, s-d and d-d contribution from the corresponding partial waves inside the AS that lead to the aspherical charge density [12]. The related charge-density coefficient  $\rho_2^0(r)$  can be obtained from the wave functions inside the AS by (in a shorthand notation)

$$\rho_2^0(r) = \sum_{E_{\mathbf{k}n} < E_F} \sum_{l,m} \sum_{l',m'} R_{lm}^{\mathbf{k}n}(r) R_{l'm'}^{\mathbf{k}n}(r) G_{2ll'}^{0mm'} \quad (4)$$

where  $G_{2ll'}^{0mm'}$  are Gaunt numbers and  $R_{lm}^{\mathbf{k}n}(r)$  denote the APW+lo radial wave functions (of state  $|\mathbf{k}n\rangle$ ) in the standard notation [8], [12] and the label (e.g. s-d) is short for  $ll'$ . For the chosen wave functions  $R_{lm}^{\mathbf{k}n}(r)$

we calculate using equation (3) the on-site Coulomb contribution to the second order CF parameter, which originate from the pair of APW+lo.

CFP (K)	$A_2^0\langle r^2 \rangle$	$A_4^0\langle r^4 \rangle$	$A_4^4\langle r^4 \rangle$	$A_6^0\langle r^6 \rangle$	$A_6^4\langle r^6 \rangle$
set A	-238	57	-1069	-47	551
set B	-32	0.9	131	19	-183
set C	-18	65	250	50	-280

CF parameters (in kelvin) from Gasser et al. [6] (set A), first principles DFT calculations (set B) and parameter search method (set C).

The densities of electronic states of NdNi<sub>2</sub>B<sub>2</sub>C have been published [9] and thus need not to be shown again. The CF parameters were obtained for NdNi<sub>2</sub>B<sub>2</sub>C from equation eq. 2. In this case the CF of tetragonal symmetry splits the J = 9/2 state of Nd into five doublets. Diagonalizing the CF hamiltonian (see eq. (1)) with the computed CF parameters yields the CF level scheme (called set B). This level scheme is compared with those derived by extrapolation from the heavy rare earth borocarbides [6] and a third set introduced below. The DFT level scheme set B has a smaller total CF splitting as the extrapolated one - set A (125.5 K compare to 492 K), but differs mainly in the lower lying CF states. Whereas parameter set B provides almost equally spaced doublets (  $\Delta_1 = 38$  K,  $\Delta_2 = 82.7$  K,  $\Delta_3 = 114$  K and  $\Delta_4 = 125.5$  K) the level scheme set A from Ref. [6] leads to two doublets ( $\Delta_1 = 33$  K) and the energy gap ( $\Delta_2 = 183.3$  K). This contradiction can be resolved using the specific heat data where the magnetic specific heat contribution is obtained by subtracting the specific heat of LaNi<sub>2</sub>B<sub>2</sub>C. We clearly observe a sharp anomaly due to antiferromagnetic ordering at T<sub>N</sub> = 4.8 K as found in neutron diffraction studies [13]. The magnetic entropy derived from the magnetic specific heat data supports an isolated doublet as the CF ground state. In addition we resolve a Schottky type anomaly centered around 50 K. The calculated Schottky contribution obtained from the DFT-CF parameters exhibits one maximum centered around 35 K whereas the calculation using the extrapolated CF parameters from [6] provides 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. This fact suggests that our DFT CF parameters (set B) can be used as good starting values for the analysis of the experimental data. It can be seen that our CF parameters provides a better description of the Schottky anomaly, which is clearly demonstrated after the subtraction of the LaNi<sub>2</sub>B<sub>2</sub>C data. On the other hand, there is a discrepancy between the position of the maximum of the calculated DFT Schottky anomaly and the experimental one. Therefore we apply a parameter space searching method to improve the agreement between theory and experiment (set C). After that procedure both maxima coincide but for temperatures above the Schottky maximum the calculated curve is still higher than the experimental one. This fact can be ascribed to the simple subtraction of the LaNi<sub>2</sub>B<sub>2</sub>C data from the NdNi<sub>2</sub>B<sub>2</sub>C data. It becomes apparent, since the derived magnetic entropy for the Nd<sup>3+</sup> ion does not approach the R ln(10) limit. We have also calculated the polycrystalline magnetic susceptibility by simply taking the average  $\chi = 1/3(\chi_a + \chi_b + \chi_c)$ . The theoretical curve is in fair agreement with the experimental one up to 200 K. The change in slope in the paramagnetic range below 20 K, which is shown in both curves, can be ascribed to the existence of a rather isolated ground state CF doublet.

According to the results of the elastic neutron scattering experiment [13] the direction of Nd magnetic moments is along the a-axis. This fact implies the negative value of the  $A_2^0\langle r^2 \rangle$  CF parameter in agreement with the results of our first principles calculations. From our results one can argue that there is a large cancellation between the Coulomb and exchange correlation contributions and between the on-site Coulomb and the lattice Coulomb contributions. We find that the main contributions to the on-

site Coulomb term come from the diagonal p-p, f-f and off-diagonal p-f and d-g contributions. The decomposition into the contributions from the different orbitals slightly depends on the choice of  $R_{MT}$  but the main features described above remain. Note, that for the decomposition of the Coulomb on-site CF parameter the contributions up to h-h terms should be calculated in contrast to the electric field gradient, where the contributions up to f-f terms are sufficient [9].

In summary we calculated the CF interaction for  $\text{NdNi}_2\text{B}_2\text{C}$  using a first principles DFT method. We demonstrated that our approach can be used to estimate the CF parameters, CF energies and various experimental data, which are in fair agreement with experiment. It would be interesting to perform inelastic neutron scattering experiments on  $\text{NdNi}_2\text{B}_2\text{C}$ , since according to our calculations (using DFT CF parameters) all four CF excitations from the CF ground state should be visible at temperatures above the magnetic ordering (e.g.  $T = 20$  K).

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