

## Effect of Magnetism on Superconductivity in Rare-Earth Compounds $\text{RENi}_2\text{B}_2\text{C}$

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### ABSTRACT

Spin-polarized first-principles density-functional electronic structure calculations were performed for 73-atoms embedded-clusters representing antiferromagnetic  $\text{RENi}_2\text{B}_2\text{C}$  (RE=Pr, Nd, Sm, Gd, Ho, Tm). A substantial difference in the extent of the exchange-polarization of the conduction electrons between early and late rare-earth compounds is revealed. This result is believed to be relevant to phenomena of coexistence of superconductivity and magnetism in these compounds.

**Key-words:** Superconductors; Rare-earth; Antiferromagnetic.

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The recent discovery of superconductivity in rare-earth quaternary compounds  $\text{RENi}_2\text{B}_2\text{C}$  ( $\text{RE} = \text{rare-earth}$ ) [1] has inspired much work regarding the interplay of magnetism and superconductivity. These tetragonal compounds, which crystallize as a variant of the  $\text{ThCr}_2\text{Si}_2$ -type structure, have complex structures with the RE atoms and C forming layers which are alternated with B and Ni layers. However, in spite of this highly anisotropic crystal structure,  $\text{LuNi}_2\text{B}_2\text{C}$  was found to be a strongly 3D metal by band structure calculations [2], with all atoms contributing to the metallic character. Furthermore, torque magnetometry experiments in the superconducting state of non-magnetic  $\text{YNi}_2\text{B}_2\text{C}$  indicated that the superconducting effective mass in this material is remarkably isotropic [3]. The somewhat higher anisotropy factors found by critical field measurements in single crystals of magnetic rare-earth compounds [4] may thus be ascribed to magnetic anisotropy due to the layers of localized spins [3]. The coherence length  $\xi$  is estimated to be of the order of  $10^2 \text{ \AA}$  [4]-[6].

Although the compounds  $\text{RENi}_2\text{B}_2\text{C}$  can be made across the whole RE series, only for the later rare-earths they are superconducting [7]. In Table I are given the values of the superconducting transition temperatures  $T_c$  and the magnetic ordering temperatures  $T_M$  [1],[4],[8]-[12]. The compounds in which magnetism coexists with superconductivity are for  $\text{RE} = \text{Dy, Ho, Er}$  and  $\text{Tm}$ . In all cases, antiferromagnetic (AFM) order is present among the layers of RE atoms. For Ho, Er and Tm the AFM transition temperature  $T_M$ , as seen in Table I, is lower than  $T_c$ ; for Dy, it is higher, so that the onset of superconductivity occurs already in the AFM ordered phase. Neutron scattering experiments on single crystals of  $\text{DyNi}_2\text{B}_2\text{C}$  revealed that below  $T_M$  this compound is a simple collinear antiferromagnet, in which the moments are aligned ferromagnetically in each rare-earth carbon layer perpendicular to the c-axis, with the RE magnetic moments of two consecutive layers aligned in opposite directions [13]. The same spin arrangement is present below 4.7K in  $\text{HoNi}_2\text{B}_2\text{C}$ , as seen also by single-crystal neutron diffraction [9]; however, between 4.7 and 6K an incommensurate modulated magnetic structure is found. At this temperature interval, reentrant behavior is observed. Neutron-diffraction studies on  $\text{ErNi}_4\text{B}_2\text{C}$  showed that this compound is in an incommensurate modulated magnetic state that coexists with superconductivity [14].

Although magnetism is known to have a destructive effect on superconductivity [15], the possibility of coexistence of superconductivity with AFM order has been demonstrated theoretically by Baltensperger and Strässler [16]. However, a detailed understanding of the interplay between superconductivity and magnetism in the  $\text{RENi}_2\text{B}_2\text{C}$  compounds remains to be achieved. The trends in  $T_c$  and  $T_M$  have been related to the de Gennes factor  $(g-1)^2J(J+1)$  of the rare-earths [8]; alternatively,  $T_c$  and  $T_M$  have been scaled to the ionic radius of the heavier rare-earths, which decreases along the series due to the well-known Lanthanide contraction [17]. However, an atomic-level understanding of how magnetism affects superconductivity in these compounds is still to be accomplished.

To address this issue, we have performed self-consistent spin-polarized first-principles electronic structure calculations for large embedded clusters (73 atoms) representing the compounds  $\text{RENi}_2\text{B}_2\text{C}$  ( $\text{RE} = \text{Pr, Nd, Sm, Gd, Ho, Tm}$ ) (see Fig. 1). The Discrete Variational method (DVM) was employed, as described extensively in the literature [18], [19]. The local density approximation was used, with the exchange-correlation potential derived by von Barth-Hedin [20]. The cluster spin-orbitals  $\phi_{i\sigma}$  are expanded on a basis of

symmetrized numerical atomic orbitals  $\chi_j^s$ :

$$\phi_{i\sigma}(\vec{r}) = \sum_j \chi_j^s(\vec{r}) C_j^i \quad (1)$$

and are employed to define the charge density of spin  $\sigma$  at the cluster

$$\rho_\sigma(\vec{r}) = \sum_i n_{i\sigma} |\phi_{i\sigma}(\vec{r})|^2 \quad , \quad (2)$$

(where  $n_{i\sigma}$  is the occupation of spin-orbital  $\phi_{i\sigma}$ ) and thus the spin-density  $[\rho_\uparrow(\vec{r}) - \rho_\downarrow(\vec{r})]$ .

In solving the Kohn-Sham equations in a three-dimensional grid of points, generated by the pseudo-random Diophantine method [18], the variational method leads to the conventional secular equations. These were solved self-consistently in a grid of  $\sim 45,000$  points. The clusters are embedded in the charge densities of several shells of neighbor atoms in the crystal, obtained by numerical atomic local density calculations. The external charge densities for each spin that penetrate the cluster region are added to the cluster density, in the construction of the Kohn-Sham hamiltonian. The Madelung potential is taken into account through Ewald summations. A model potential is used, with a model density constructed with overlapping spherical functions centered at the atomic nuclei, and fitted to the true density in each iteration by a least-squares procedure.

Only the valence orbitals of the atoms were kept in the variational space, the core orbitals being ‘‘frozen’’ after the first iteration. These are 3s, 3p, 3d, 4s and 4p for Ni, and 4f, 5s, 5p, 5d, 6s and 6p for the RE. We considered important to keep the 4f orbital in the valence to allow for hybridization of this orbital with the 5d, 6s and 6p of the RE, and to obtain the self-consistent 4f occupation in the solid. The 2s and 2p orbitals of C and B were kept in the valence. Interatomic distances were obtained from crystallographic data reported in the literature [1], [12], [21] except for  $\text{PrNi}_2\text{B}_2\text{C}$  and  $\text{NdNi}_2\text{B}_2\text{C}$  in which case the distances were estimated by extrapolation from the data for the other rare-earth compounds.

In our calculations we adopted the simple collinear AFM structure in all cases; thus in Fig. 1 all the RE atoms on the RE–C plane with  $z > 0$  have positive spin moments, and negative moments on the  $z < 0$  plane (defining the Ni plane as  $z = 0$ ). The calculated spin magnetic moments  $\mu$  on the RE atom, defined as the difference between spin  $\uparrow$  and spin  $\downarrow$  Mulliken populations, are 2.40 for Pr, 3.62 for Nd, 5.83 for Sm, 6.65 for Gd, 3.16 for Ho and 0.83 for Tm (in  $\mu_B$ ). Most of this moment is due to the 4f orbital, although small contributions from the 5d (predominantly), 6s and 6p are present. The small 5d moments align ferromagnetically with 4f, and the 6p antiferromagnetically. The 6s moments are negligibly small or zero in all cases. A small moment develops on the C atoms by polarization; this is negative for the lighter rare-earths up to Gd, then turns positive for Ho and Tm. Small positive moments are present on B; on Ni the moments are zero due to the magnetic symmetry.

From the calculations was obtained the spin density at point  $\vec{r}$   $[\rho_\uparrow(\vec{r}) - \rho_\downarrow(\vec{r})]$ . The spin-density spatial distribution was found to be strikingly different in the lighter and heavier rare-earth compounds. The reason for this is the following: The 4f electrons polarize the valence (preponderantly the 5d) by exchange interactions; this polarization is extended to the valence electrons of the other atoms in the crystal. Along the Lanthanide

series there is a decrease of the 4f radius  $R(4f)$ , as well as of the radii of the RE valence orbitals; however, the contraction of the 4f orbital is considerably more pronounced along the series (due to the proximity with the nucleus) than that of 5d, such that the *difference*  $[R(5d) - R(4f)]$  increases from lighter to heavier rare-earths. This trend may be observed by atomic self-consistent calculations, and has been related to magnetic properties of RE intermetallics [22]. Thus the exchange polarization of the conduction electrons by the 4f spin moment will be more effective in the lighter than in the heavier rare-earths.

To illustrate this effect, we selected spin-density maps for  $\text{NdNi}_2\text{B}_2\text{C}$  and  $\text{HoNi}_2\text{B}_2\text{C}$ , in which the lighter RE Nd (configuration  $4f^{3.68}$  in the calculation) and heavier Ho ( $4f^{10.79}$ ) have comparable 4f spin moments ( $3.59\mu_B$  for Nd, and  $3.14\mu_B$  for Ho). These are shown in Figs. 2a and 2b in a diagonal plane along the c direction, which includes RE and C atoms in the upper RE–C plane (see Fig. 1) and in the lower plane, with antiparallel spins. This plane was chosen since it includes atoms in the interior of the cluster, to avoid the small spurious surface effects found in the external atoms. These figures show clearly the pronounced difference in the conduction electrons spin polarization between the two compounds, which is spatially more extended for  $\text{NdNi}_2\text{B}_2\text{C}$ . In Fig. 2a is also seen the AFM polarization of the C atoms in this latter compound, characterizing a superexchange-type interaction between Nd and C. This same feature is present for  $\text{PrNi}_2\text{B}_2\text{C}$ ,  $\text{SmNi}_2\text{B}_2\text{C}$  and  $\text{GdNi}_2\text{B}_2\text{C}$ , consistent with the negative magnetic moments found on C by the Mulliken analysis mentioned earlier. For  $\text{HoNi}_2\text{B}_2\text{C}$  and  $\text{TmNi}_2\text{B}_2\text{C}$ , the spin moments on C change sign, as may be seen from the contours on Fig. 2b for the Ho compound, and consistent with Mulliken analysis. The polarization on B is very small. In Figures 3a and 3b the valence electrons spin densities of the same compounds is shown on the (011) plane, which includes Ni atoms. Again the striking difference in the conduction electrons spin polarization of the two compounds is made evident.

For comparison purposes, we may consider the spin-polarization field given by [23]:

$$H = (8\pi/3)\mu_B[\rho_{\uparrow}(\vec{r}) - \rho_{\downarrow}(\vec{r})] \equiv 524.3\Delta\rho(\vec{r})kG \quad (3)$$

The existence of such field may be considered to constitute one of the mechanisms of Cooper-pair breaking.

In Fig. 4 is shown the spin-polarization field, as defined in Eq. (3), along lines joining neighbor atoms in the sequence  $\text{RE}\uparrow - \text{C} - \text{B} - \text{Ni} - \text{B} - \text{C} - \text{RE}\downarrow$ , that is, from the upper RE–C plane to the lower (see Fig. 1), for all the compounds investigated.

It is seen that even Pr, which has a considerably smaller 4f spin moment ( $2.37\mu_B$ ) than Ho ( $3.14\mu_B$ ), polarizes the conduction electrons more effectively than the latter, due to a smaller difference between  $R(5d)$  and  $R(4f)$ . We may observe also that Sm ( $\mu(4f)=5.79\mu_B$ ) polarizes the C atoms considerably more than Gd which has a larger 4f moment ( $6.57\mu_B$ ); in fact, the C polarization due to Gd scales with that due to Nd, with only  $3.59\mu_B$  for the 4f spin moment, but with a smaller  $[R(5d) - R(4f)]$ .

In view of these results, we propose that the differences found in the spin polarization of the conduction electrons along the Lanthanide series in the  $\text{RENi}_2\text{B}_2\text{C}$  compounds are relevant in explaining the coexistence or not of magnetism and superconductivity. Since the superconductivity in these compounds is quite isotropic, as mentioned earlier, it may be affected by the polarization field in any direction. Thus differences in the extent of the spin polarization may be an important factor in explaining why a late rare-

earth compound shows coexistence of antiferromagnetism and superconductivity while an earlier rare-earth compound with comparable RE moment does not, as well as the trend in  $T_c$  (Table I). Another experimental result which may be related to this effect is the much more effective suppression of  $T_c$  in  $\text{YNi}_2\text{B}_2\text{C}$ , caused by substitution by Sm in  $(\text{Y}_{1-x}\text{Sm}_x)\text{Ni}_2\text{B}_2\text{C}$ , as compared to  $(\text{Y}_{1-x}\text{Dy}_x)\text{Ni}_2\text{B}_2\text{C}$  [24]. This happens in spite of the smaller de Gennes factor (4.5) of Sm, as compared to Dy (7.1), and may be ascribed to a smaller difference between R(5d) and R(4f), and thus more extensive polarization of the valence electrons, in the earlier rare earth.

Finally, we point out that differences in the extent of the conduction-electrons spin-polarization along the Lanthanide series should be present in other RE compounds in which superconductivity may coexist with magnetism, and thus should be taken into account when attempting to understand the interplay of these phenomena.

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Table CaptionTable I

Superconducting critical temperatures  $T_c$  and AFM ordering temperatures  $T_M$  for  $\text{RENi}_2\text{B}_2\text{C}$  compounds.

- a) From Ref. (8)
- b) From Ref. (9)
- c) From Ref. (10)
- d) From Ref. (11)
- e) From Ref. (4)
- f) From Ref. (1)
- g) From Ref. (12)
- h) From Ref. (8)

Figure Captions

Figure 1: 73-atoms cluster representing  $\text{RENi}_2\text{B}_2\text{C}$  compounds. The Ni plane is defined as  $z=0$ .

Figure 2a: Spin density  $[\rho_\uparrow(\vec{r}) - \rho_\downarrow(\vec{r})]$  contours on a diagonal plane along the  $c$  direction for  $\text{NdNi}_2\text{B}_2\text{C}$ . Contours are from  $-0.002$  to  $+0.002$   $e/\text{au}^3$  with intervals of  $0.0001$   $e/\text{au}^3$ . Alternatively, contours are from  $\sim -1.05\text{kG}$  to  $+1.05\text{kG}$  with intervals of  $\sim 0.05\text{kG}$ , employing Eq. 3. Full lines are positive values.

Figure 2b: Spin density contours on a diagonal plane along the  $c$  direction for  $\text{HoNi}_2\text{B}_2\text{C}$ . Contour specifications as in Fig. 2a.

Figure 3a: Spin density contours on the (011) plane for  $\text{NdNi}_2\text{B}_2\text{C}$ . Contour specifications as in Fig. 2a.

Figure 3b: Spin density contours on the (011) plane for  $\text{HoNi}_2\text{B}_2\text{C}$ . Contour specifications as in Fig. 2a.

Figure 4: Polarization field  $H$ , as defined in Eq. 3, along the line joining the nuclei of neighbor atoms in the sequence  $\text{RE}\uparrow - \text{C} - \text{B} - \text{Ni} - \text{B} - \text{C} - \text{RE}\downarrow$  (from the  $z > 0$   $\text{RE}-\text{C}$  plane to the  $z < 0$   $\text{RE}-\text{C}$  plane), for the compounds  $\text{RENi}_2\text{B}_2\text{C}$  investigated.

Table I

RE	$T_c$ (K)	$T_M$ (K)
Sm	-	9.9 <sup>(g)</sup>
Gd	-	20 <sup>(h)</sup>
Tb	-	15 <sup>(h)</sup>
Dy	6.2 <sup>(a)</sup>	10.3 <sup>(a)</sup>
Ho	8.0 <sup>(b)</sup>	6 <sup>(b)</sup>
	7.5 <sup>(c)</sup>	8 <sup>(c)</sup>
Er	10.5 <sup>(d)</sup>	5.9 <sup>(d)</sup>
Tm	11 <sup>(e)</sup>	1.5 <sup>(e)</sup>
Y	15.6 <sup>(f)</sup>	-
Lu	16.6 <sup>(f)</sup>	-

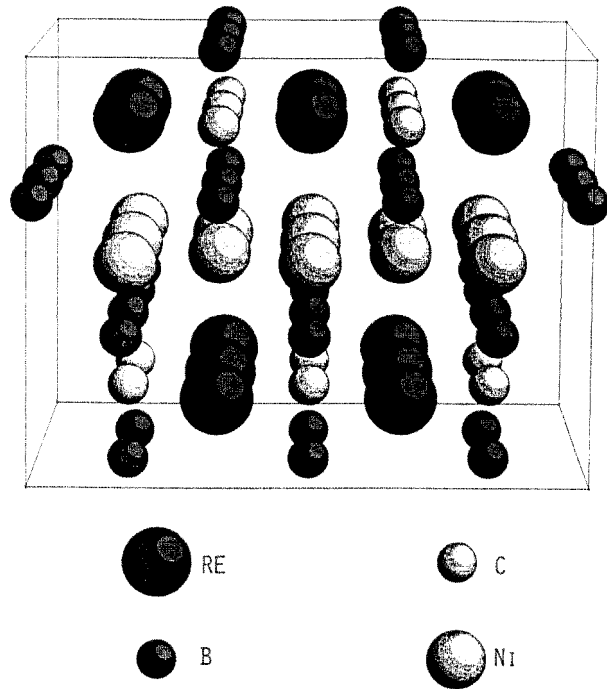
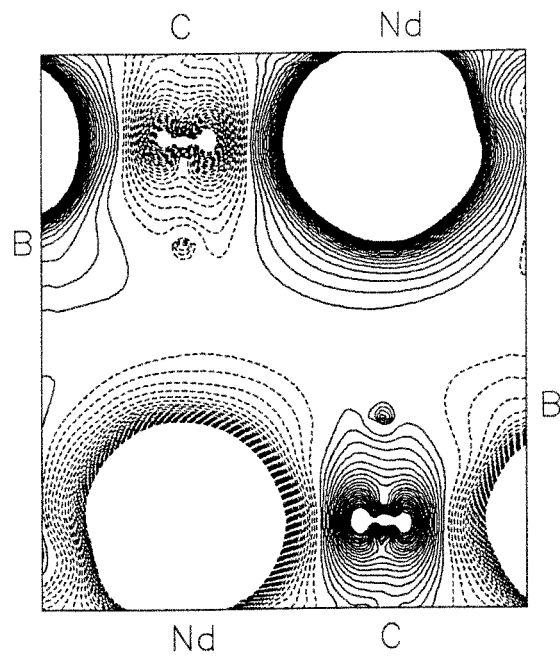
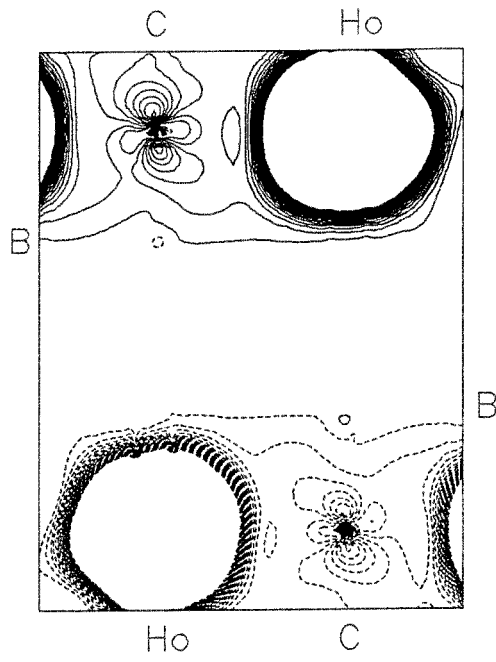


Fig. 1



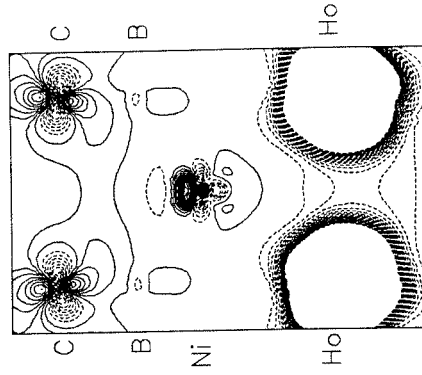


2a

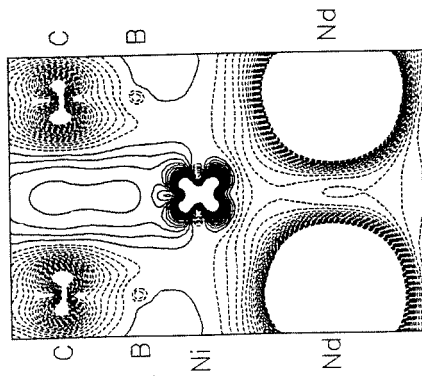


2b

3b



3a



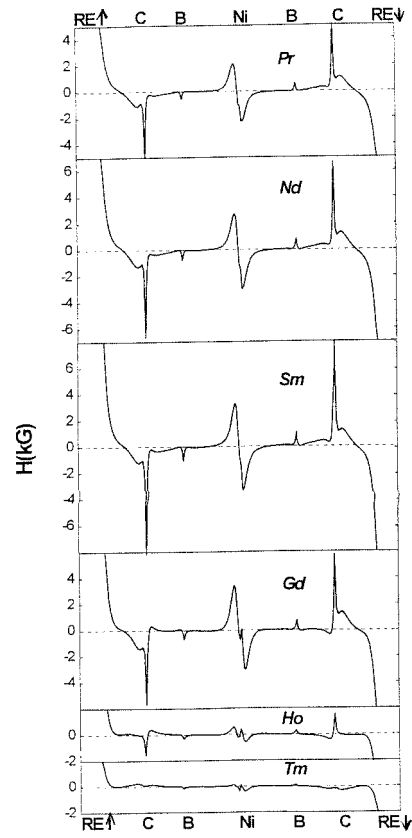


Fig. 4

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