Electronic Structure of the $RENi_2B_2C$ Superconductor

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A recent report of superconductivity in the $RENi_2B_2C$ systems, with a T_c as high as 16.6 K for RE = Lu,[1] immediately prompts several theoretical questions. For example, what do the densities of states of these compounds look like near the Fermi level? BCS theory[2] associates high critical superconducting temperatures with a high density of states at the Fermi level.[3] Why is LuNiBC, with a related structure, not superconducting? In this communication we show how the computed electronic densities of states influence the properties of these new compounds.

The structure of the new materials[4] is a derivative of the well-known $ThCr_2Si_2$-type structure. The boron atoms from adjacent layers of Ni_2B_2 are connected via carbon atoms, and the cavities are occupied by the rare-earth cations. Another way of viewing the structure is as being built of alternating layers of Ni_2B_2 and REC. The parent structure has received much theoretical interest and formed the basis of an interesting exposition concerning the derivation and understanding of the band structures of the solids.[5] However the electronic picture derived for the silicides and phosphides with this structure differs considerably from that of the present systems. Experience with the band structures of metal borides,[6] where metal 3d and boron 2p levels are close in energy, tells us that the form of the band structure from a tight-binding calculation will be very sensitive to the values chosen for the metal and boron H_{ii} parameters and that the dispersion picture is considerably more complex than those cases where there is a significant separation between atomic metal and non-metal levels. To this end, we have carried out tight-binding calculations within the extended Hückel ansatz (EHTB) and first principles self-consistent linear muffin-tin orbital (LMTO) calculations[7-9] to ensure that the electronic picture we present is a reliable one.[10]

Figure 1 shows the total and partial densities of states calculated by the LMTO method, and Figure 2 shows the total density of states calculated by the EHTB method. Y instead of Lu was used for the calculations since its extended Hückel parameters are perhaps more reliable.[11]

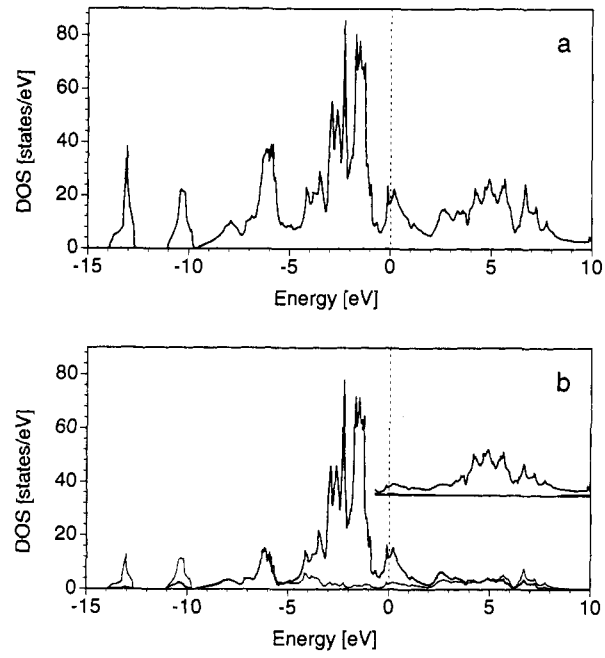

Figure 1. Densities of states of YNi_2B_2C calculated by the LMTO method: (a) total density of states; (b) the Ni (thick line) and B (thin line) partial densities of states. Also shown at right is the Y partial densities of states. There is no carbon contribution at the Fermi level shown by a broken line.

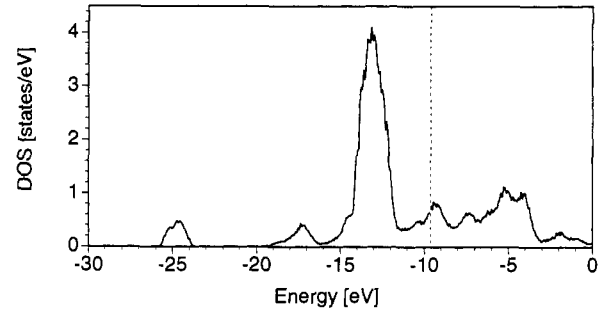

Figure 2. Total density of states of YNi_2B_2C calculated by the EHTB method. The Fermi level is shown by a broken line.

The DOS from the two methods are quite similar around the Fermi level but quite different at deeper energies. The two lowest in energy bands are of mostly C s and B s character, respectively (around –13 and –10 eV and around –25 and –17 eV on Figures 1 and 2, respectively). The peak around –6 eV in the LMTO DOS of Figure 1 is hidden underneath the large peak around –13 eV in the EHTB DOS of Figure 2 and contains mostly C and B p states. The largest peaks in both figures correspond to the Ni d states. The relatively wide bands above the Fermi level are the rare-earth d bands. The Fermi level lies close to a peak in both calculations. As can be seen from the partial densities of states

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(10) The relativistic LMTO calculations were done with the atomic sphere approximation with the following Wigner-Seitz radii for the components: Y - 1.799, Ni - 1.349, B, 1.164; C, 1.111. The wave functions for Y and Ni were expanded through $l = 2$, and those for B and C, through $l = 1$. The exponents (ζ) and the valence shell ionization potentials (H_{ii} in eV) for the EHTB calculations were respectively as follows: 1.3, –15.2 for B 2s; 1.3, –8.5 for B 2p; 1.63, –21.4 for C 2s; 1.63, –11.4 for C 2p; 1.39, –8.6 for Y 5s; 1.39, –5.0 for Y 5p; 1.93, –8.86 for Ni 4s; 1.93, –4.90 for Ni 4p. Double-ζ expansion was used for the d orbitals of Y and Ni. The exponents, the weighting coefficients, and the ionization potentials were respectively as follow: $\zeta_1 = 4.33$, $\zeta_2 = 1.4$, $C_1 = 0.5827$, $C_2 = 0.6772$, $H_{ii} = -8.4$ eV for Y; $\zeta_1 = 5.75$, $\zeta_2 = 2.20$, $C_1 = 0.5817$, $C_2 = 0.5800$, $H_{ii} = -12.99$ eV for Ni.

(11) YNi_2B_2C is superconducting, as well, with $T_c = 15.6$ K.[1]

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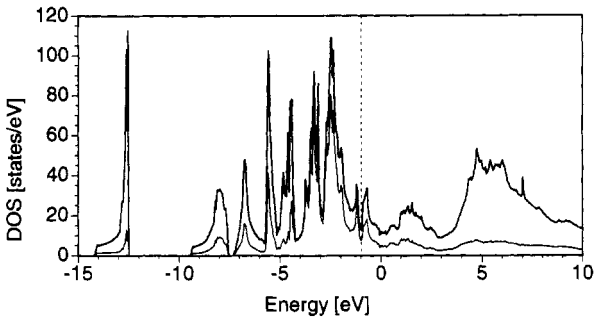

Figure 3. Total density of states (thick line) and the Ni partial density of states (thin line) of YNiBC calculated by the LMTO method. The Fermi level is shown by a broken line.

in Figure 1, this peak is predominantly of Ni character but also contains some boron and yttrium character. Only carbon states are not present. The different positions of the deeper lying bands using the different methods may be understood by noting the shifts expected in the extended Hückel levels once the charge is included. The charges on the atoms derived from the latter, positive on Y and B and negative on Ni and C, suggest that the Ni and C atomic levels should be chosen slightly higher in energy and those for the B atoms, slightly lower. This would make the two pictures much closer in appearance.

The fact that the Fermi level is quite close to a peak in the density of states for these compounds suggests that in the superconducting phase it actually coincides with the peak. From the EHTB calculations we find that an additional ~0.5 electron per formula unit is needed to optimally move the Fermi level. This would correspond to removal of ~0.125 carbon atom, a defect level virtually impossible to detect by standard X-ray crystallographic means for this system. Since borides with the $ThCr_2Si_2$ structure exist without carbon and show long (nonbonding) B–B distances (2.28 Å in YCo_2B_2, as an example), the speculation that some carbon atoms may be missing in the superconducting materials (B–B distance of ~2.9 Å) is a reasonable one. Moreover, another superconducting compound, $YPd_5B_3C_{0.3}$ (T_c = 23 K), with similar composition but undetermined structure, seems to be nonstoichiometric in its carbon content only.[12]

The fine structure at the Fermi level in the densities of states shows up most clearly in the LMTO results of Figure 1. A rigid band model shows that addition of ~0.6 electron or removal of ~0.47 electron would cause the Fermi level to coincide with the two peaks close to it. This corresponds to removal of 0.15 carbon or 0.16 yttrium atom, respectively.

In order to determine to what extent the yttrium can be considered simply as a cation, we performed EHTB calculations on $Ni_2B_2C^{3-}$. The DOS from these calculations look very similar in shape to that of YNi_2B_2C, but the position of the Fermi level is higher in energy by ~0.7 eV and is above the peak near the Fermi level in Figures 1 and 2. This shows that there is substantial mixing of Y states below the Fermi level, in fact with states on carbon. This is also suggested by the similar shapes of the partial densities of states for Y and C around –6 eV in Figure 1. All this, in turn, suggests that the yttrium–carbon interactions may be crucial for the right positioning of the Fermi level in order to achieve a superconducting state. Additional LMTO calculations performed with Lu instead of Y showed only a small difference in the DOS above –5 eV, where little or no C character is present, very little change in the Fermi level positioning, and an increase in the density of states at the Fermi level of about 3%.

The structure of the non-superconducting YNiBC is similar to that of YNi_2B_2C, but instead of one it has two layers of YC between every two layers of Ni_2B_2. Figure 3 shows the total and partial densities of states for this compound calculated by the LMTO method. The Fermi level is in a well-defined valley between two very sharp peaks due mainly to Ni states but in a region where there is noticeable contribution from yttrium and boron levels. This positioning of the Fermi level may be why this compound is not superconducting. In a fashion similar to that used for YNi_2B_2C, one can calculate how many electrons are needed to reach any of the adjacent peaks. The results are one-third additional electrons or one-half of the electrons removed. These correspond to one-twelfth of the carbon or one-sixth of the yttrium atoms missing, respectively. The magnitude of these defects is similar to that for YNi_2B_2C.

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