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The electronic structure of the new cubic carbaboride NaB_5C as compared to CaB_6 and 'B_4C_2' by the full-potential LMTO method

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The full-potential LMTO (FP LMTO) method was used for the first time to examine the electronic properties and chemical bonding of the new carbaboride NaB_5C in comparison with isostructural and isoelectronic hexaboride CaB_6 and 'B_4C_2'.

Metal hexaborides (MB_6) exhibit interesting physical and chemical properties. They are used as materials for high-temperature applications and are intensively studied both theoretically and experimentally.[1,2] Extensive investigations of the modification of properties of binary hexaborides are under way. A conventional technique is the doping of the cation sublattice of MB_6 with metal atoms (M′). For example, ternary phases such as rare-earth metal–doped CaB_6 ($Ca_{1-x}LaB_6$,[3] $Ca_{1-x}Eu_xB_6$,[4] *etc.*) are well known.

An alternative way of changing the properties of binary hexaborides is the doping of their boron sublattice. A new group of ternary boron-rich compounds (NaB_5C and KB_5C) has been synthesised recently.[5] They crystallise in a cubic (space group O_h^1–$Pm3m$) CaB_6-like structure where carbon atoms statistically replace boron atoms in B_6 octahedra. As distinct from metal-like NaB_6 and KB_6, these new compounds (carbaborides) are semiconductors.[5]

Table 1 Electronic structure parameters of cubic CaB_6, NaB_5C and 'B_4C_2' (Ry).

Parameter/ phase	Forbidden gap (transition)	Band widths		
		Hybrid *sp*	B 2*s*	Energy gap (*sp*–B 2*s*)
CaB_6	0.048 (X → X)	0.664	0.080	0.328
NaB_5C	0.120 (Γ → X)	0.792	0.056	0.304
'B_4C_2'	0.125 (Γ → X)	0.992	0.041	0.261

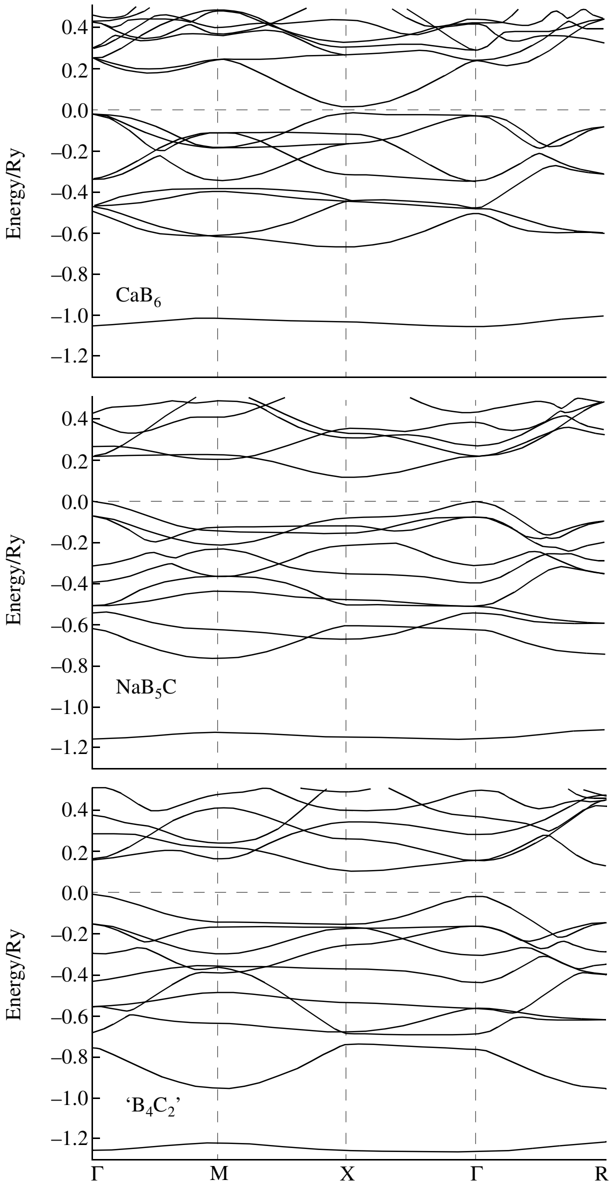

Figure 1 Energy bands of CaB_6, NaB_5C and 'B_4C_2'.

In this communication, we report the first findings of the electronic state investigations of a new phase, hexagonal NaB_5C, and compare them with the electronic states of isostructural and isoelectronic phases of thoroughly studied CaB_6,[2,6–8] as well as with the hypothetical 'carbaboride' B_4C_2. The latter compound represents the structure model of a CaC_6-like boride, in which the cation sublattice is 'empty' and one third of boron atoms in the anion sublattice is replaced by carbon atoms. The calculation of 'B_4C_2' makes it possible to follow the tendencies in changing the electronic spectra of hexaborides when the C/B ratio increases and to establish the role of cationic vacancies. It is well known that these lattice defects are present in some hexaborides.[1,2] Recently, Mair *et al.*[9] reported the synthesis of dilithium hexaboride. The structure of Li_2B_6 is of the CaB_6 type with the incomplete occupancy of cationic positions. This favours the appearance of Li^+-ionic conductivity. However, the role of cationic vacancies in the formation of the electronic spectra of hexaborides has not been studied until the present time.

The electronic structure of CaB_6, NaB_5C and 'B_4C_2' was calculated by the self-consistent full-potential linear muffin-tin orbital method (FP LMTO)[10,11] in the local electronic density approximation.[12] The computational procedure was described in detail elsewhere.[13] The lattice parameter corresponded to $a(CaB_6) = 7.8352$ a.u.[1]

The energy bands and densities of states (DOS) of CaB_6, NaB_5C and 'B_4C_2' are given in Figures 1 and 2, and the parameters of electronic structures are listed in Table 1.

The common valence band of CaB_6 (width of ~1.07 Ry) contains 10 occupied energy bands. The lower quasi-core B 2*s*-like band is separated from the group of nine hybrid B 2*p*,2*s*-bands by a forbidden gap. The DOS profile of these bands has two maxima (B and B′ in Figure 2) corresponding to hybrid states, which form covalent B–B *sp*-bonds inside and between B_6 clusters. The first unoccupied band has a large wave-vector dependence, which reflects a delocalised character of the *d*-states of cations forming the lower edge of the conductivity band. This feature is typical of all CaB_6-like hexaborides.[2,6–8] The direct energy gap (ΔE_g) between the valence band and the conduction band (in the *X* point) is ~0.05 Ry (~0.7 eV).

An essentially different type of the electronic spectrum was obtained for NaB_5C (see Figures 1 and 2). Whereas the struc-

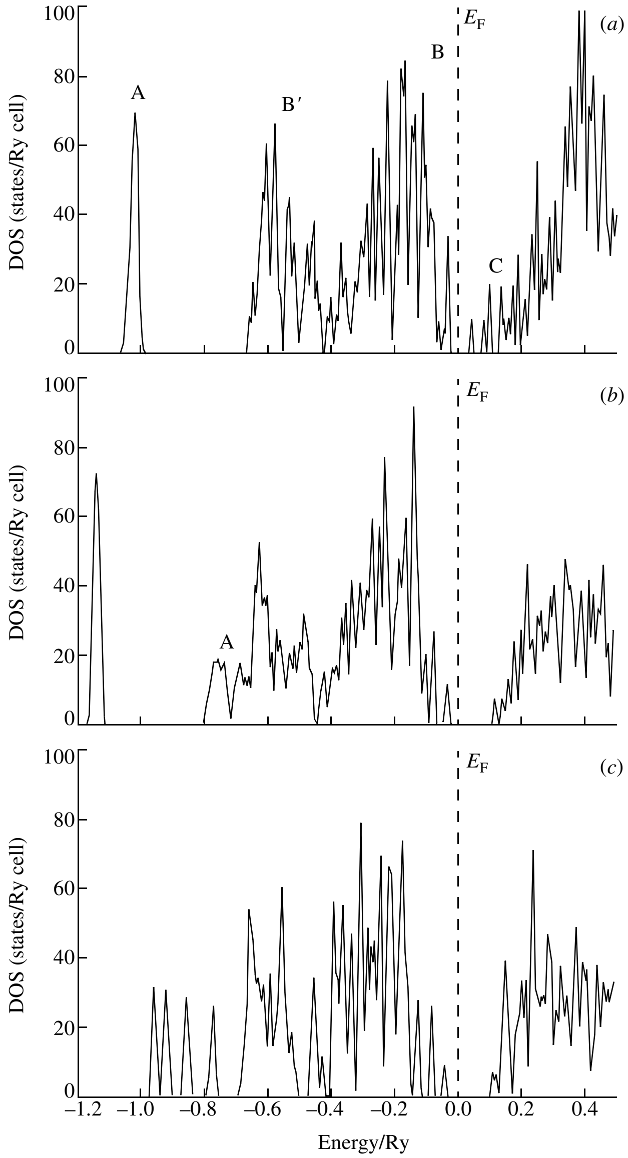

Figure 2 DOS of (*a*) CaB_6, (*b*) NaB_5C and (*c*) 'B_4C_2'.

ture of the lower edge of the conduction band of CaB_6 and NaB_5C remains generally the same (the replacement of a cation leads mainly to a decrease in the energy dispersion of the lower unoccupied band), the substitution of a carbon atom for a boron atom (in B_6 clusters) radically alters the structure of the valence band. Figures 1 and 2 and Table 1 show that for NaB_5C, as compared to CaB_6, (i) the total width of the valence band and of the hybrid *sp*-band increases; (ii) the forbidden gap between B 2*s*- and *sp*-bands decreases; (iii) the widths of B 2*s*- and B *sp*-bands decrease; and (iv) new C 2*s*- (not shown in Figures 1 and 2) and C 2*p*-bands appear. The latter bands lie in the range from 0.8 to 0.4 Ry below the Fermi level (E_F; peak A, Figure 2). The emergence of an anisotropic system of covalent B–B and B–C *sp*-bonds (inside and between B_5C clusters, see Figure 3) disrupts the quasiatomic character of some bands. For example, the upper near-Fermi band becomes energetically dispersed along the Γ–X direction (Figure 2). As a result, the type of interband transitions in CaB_6 and NaB_5C radically changes: instead of the direct gap in the hexaboride, the semiconducting state for NaB_5C is characterised by an indirect gap [Γ → X transition; $\Delta E_g \sim 0.12$ Ry (~1.63 eV)].

The type of the electronic spectrum of the hypothetical 'B_4C_2' changes as well. The increase in the C/B ratio and the appearance of direct *s*–*p* C–C bonds (Figure 3) favour further growth of the total width of the valence band, near the lower edge of which isolated C 2*p*-like states (a group of DOS peaks in the range from 0.95 to 0.75 Ry below E_F, Figure 2) emerge. The contribution of C 2*p*-states to the lower unoccupied band increases. The forbidden gap of 'B_4C_2' [indirect transition Γ → X; $\Delta E_g \sim 0.13$ Ry (~1.77 eV)] has an intermediate value between ΔE_g for the stable rhombohedral boron carbide B_4C (with icosahedral $B_{11}C$ clusters) and the higher carbon-rich BC_3 with a layered graphite-like structure.[14] To draw a conclusion on the possible stabilization of 'B_4C_2', it is necessary to solve correctly the equation of state for this phase.

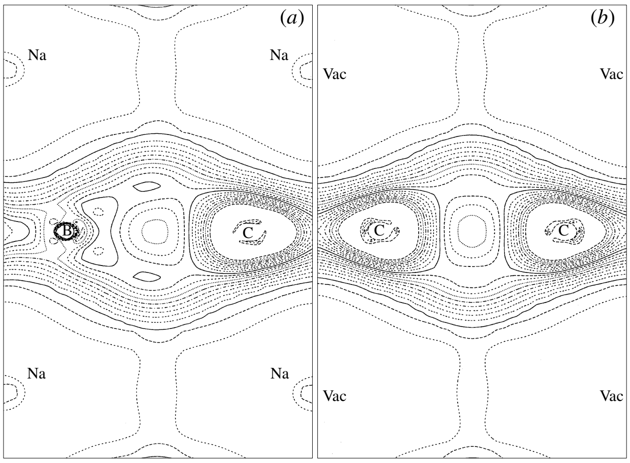

Figure 3 Valence density distribution for (*a*) NaB_5C and (*b*) 'B_4C_2'.

In summary, note that the imitation of the role of cation defects in the calculations of 'B_4C_2' with an 'empty' metallic sublattice makes it possible to arrive at the preliminary conclusion that no new occupied 'vacancy' states appear in the spectra of cation-deficient hexaborides (unlike, for example, nonstoichiometric transition metal carbides[15]). This can be seen in the electronic density maps of 'B_4C_2' (Figure 3). Qualitatively, this fact may be related to the distribution of valence states of anions (B, C), which are localised in the vicinity of nuclei and are not 'trapped' by the cation defect sphere. Hence, we can assume that the role of variable content of cation vacancies in metal hexaborides may be reduced to changes in electron concentration in the cell (*i.e.*, to changes in the degree of near-Fermi band occupation as a function of the M/B ratio), without a detectable rearrangement of the energy spectrum structure.

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