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Rapid Research Note

The Electronic Band Structures of Superconducting MgB_2 and Related Borides CaB_2, MgB_6 and CaB_6

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Introduction The discovery of superconductivity for magnesium diboride in January 2001 [1] may become an important stage in the development of superconductivity theory. As distinct from HTSC, MgB_2 has a simple composition and structure (AlB_2-type, space group P6/mmm, $Z = 1$). The transition temperature for MgB_2 ($T_C \sim 40$ K) is an intermediate one, which exceeds more than twice the record values of T_C for binary B1 or A15-type intermetallic superconductors [2].

The first-principle band structure calculation of MgB_2 was carried out by the authors [3] using the FLMTO method. It was shown that the energy bands of MgB_2 are formed due to strong B–B interactions (in honeycomb layers of boron atoms). The density of states (DOS) profile exhibits a B 2p-like DOS peak at the Fermi level.

The purpose of the present work is to study in detail the electronic band structure of MgB_2 in comparison with that of related borides: CaB_6 and hypothetical CaB_2 and MgB_6.

Computational The band structure of the above borides was calculated by the self-consistent nonempirical full-potential LMTO (FP-LMTO) method [4]. The lattice parameters of stable MgB_2 and CaB_6 (space group Pm3m) corresponded to those presented in [5]. For hypothetical phases (CaB_2, MgB_6) the lattice constants were determined by the total energy minimization. The optimizied parameters are $a = 3.205$ Å, $c/a = 1.24$ for CaB_2 and $a = 4.115$ Å for MgB_6.

Results The valence band (VB) of MgB_2 is formed predominantly by B 2p states (see Fig. 1). The dependence $E(k)$ for B $2p_{x,y}$ and $2p_z$ bands differs considerably. For B $2p_{x,y}$ like bands the most pronounced dispersion of $E(k)$ is observed in the direction $k_{x,y}$ (Γ–K). These bands are of the quasi-two-dimensional (2D) type. They form a flat zone in the direction k_z (Γ–A) and reflect the distribution of pp_σ states in the boron layers. These states make a considerable contribution to the DOS at the Fermi level ($N(E_F)$) resulting in the metallic properties of the diboride. The Fermi level is located in the region of bonding states, the conductivity of MgB_2 is due to hole carriers. Mg is ionized and the charge transfer takes place in the direction Mg → B.

The B $2p_z$-like bands are responsible for weaker pp_π interactions. Those 3D-type bands have the maximum dispersion in the direction k_z (Γ–A). Thus, the peculiarities of the electronic properties of MgB_2 are associated with metal-like 2p states of boron atoms located in plane nets, which determine the DOS distribution in the vicinity of the Fermi level.

Hirsch [6] made an assumption about the superconductivity in MgB_2 based on the theory of hole superconductivity. Kortus et al. [7] suggest that strong covalent B–B bonding should include strong electron–ion scattering and hence strong electron–phonon coupling. The authors [6, 7] believe that the superconductivity is due mainly to B $2p_{x,y}$ states. Let us compare the band structure of MgB_2 and related borides CaB_6 and hypothetical CaB_2 and MgB_6.

The band structure of isoelectronic and isostructural MgB_2 and CaB_2 phases turned out to be similar on the whole, see the figure. The main differences can be attributed to the changes in intra- and interlayer distances depending on the atomic radii ($r_c = 0.74$ (Mg) and 1.04 Å (Ca)). For CaB_2 a general narrowing (by ≈ 0.05 Ry) of B 2p-like VB takes place. B $2p_z$-like bands intersect the Fermi level at the point K. The resulting value of $N(E_F)$ (20.80) is almost twice as much as that for MgB_2 (11.44 states/Ry). An increase of hole concentration in cylinders surrounding the Γ–A line of the BZ takes place.

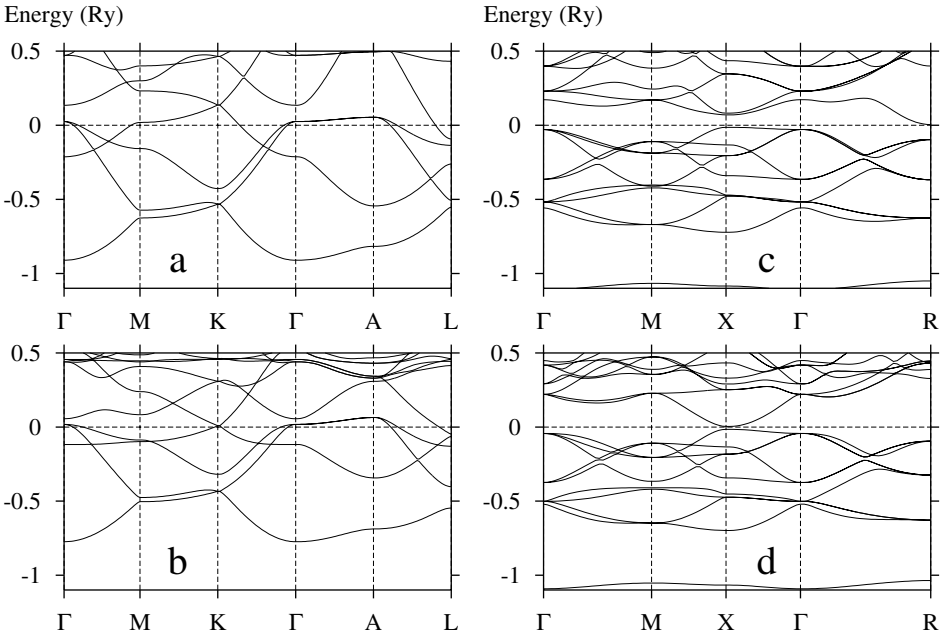

Fig. 1. Band structures of a) MgB_2, b) CaB_2, c) MgB_6 and d) CaB_6

The electronic properties of Mg, Ca hexaborides (see also [8, 9, 10]) are of quite different kind (see Fig. 1). The main elements of their structure are B_6 octahedra [2]. The ten occupied energy bands are made up by hybrid B 2s,p states that form inter- and intraoctahedral B–B bonds. The VB of CaB_2 is narrower that of MgB_2 by about 0.019 Ry. The highest occupied bands (forming a flat zone in the direction (X–Γ)) are due to B $p_{x,y}$ states that form interoctahedral bonds. The first antibonding band contains a considerable contribution from cationic states and has a large wave-vector dependence. The hexaborides are narrow-gap semiconductors with a direct band gap ($\Delta E_g \approx 0.0163$ Ry, transition at point Γ) for CaB_6 and an indirect transition ($\Delta E_g \approx 0.0150$ Ry, transition X–R) for MgB_6.

Conclusions The electronic structure of alkaline-earth metal borides is determined mainly by strong B–B interactions. However, for MB_6 and MB_2 it differs radically. The cubic phases (MB_6) are semiconductors. The peculiarities of the VB near the Fermi level are due to the dispersion of B $p_{x,y}$ bands forming B–B bonds between B_6 octahera. Hexagonal layered phases (MB_2) exhibit pronounced metal-like properties with a high density of B $2p_{x,y}$ states at the Fermi level and hole conductivity. B $2p_{x,y}$ bands are of the 2D-type and reflect the distribution of pp_σ states in plane nets of boron atoms. The above described features of the electronic structure are responsible for the appearance of the superconducting effect in MgB_2 [7]. We showed that the hypothetical CaB_2 could be the nearest analogue of MgB_2 as a MTSC. We suggest that the possible way of searching for similar MTSC should be via MgB_2 (or CaB_2) hole doping (by synthesizing ternary SS) or via creating layered superstructures (. . . /B/Ca/B/Mg/B . . .). The investigations of such systems are currently in progress.

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