Bonding nature and wave function around the Fermi level of MgB_2-related compounds

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Abstract

We present first-principles molecular-orbital calculations for the 39-K superconductor MgB_2 and related diborides using the DV-$X\alpha$ method. The electronic structure of a slab cluster embedded in the Madelung potential is determined self-consistently in terms of charge transfer between Mg and B. In contrast with the simplest ionic picture $Mg^{2+}B_2^-$, the negative charge of B is estimated to be 0.39. Our results, which include total and partial density of states, overlap population in the neighboring B-B and Mg-B bonds and wave functions around the Fermi energy E_F consisting of B $2p_{x,y}$ orbitals in the B planes, indicate the incomplete filling of the σ orbitals in MgB_2. We discuss possible ways to achieve higher transition temperatures in non-periodic systems such as surfaces, interfaces and artificially layered hetero-structures based on this approach.

Key words: diborides; electronic structure; molecular orbitals; Madelung potential

1. Introduction

There has been rapid progress in our understanding of the electronic structure of MgB_2 since the first announcement of superconductivity at 39 K [1]. In spite of the crystal-structural similarity to intercalated graphite with carbon replaced by boron, MgB_2 represents a new class of superconductors. The simplest ionic picture would suggest that the Mg donates two outer electrons to B planes. This picture is supported by recent band structure calculations [2]. Although MgB_2 is formally isoelectronic to graphite, its unique feature is the incomplete filling of σ bands corresponding to sp^2-hybridized bonding within the graphite-like B planes.

In this paper, we attempt to examine the relationship between the σ band structure in $\boldsymbol{k}$ space and the in-plane sp^2 bonding nature in real space for MgB_2 and some related diborides using first-principles molecular-orbital calculations.

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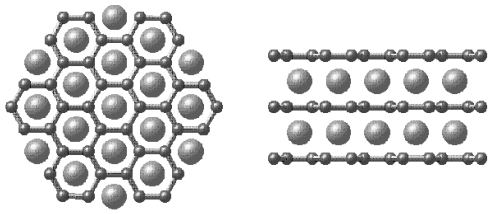

Fig. 1. Top view and cross-sectional view of our cluster model employed in the DV-$X\alpha$ calculation.

2. Calculational Methods

Our approach is based on the DV-$X\alpha$ method [3] that utilizes discrete variational (DV) integral and local density approximation ($X\alpha$). MgB_2 occurs in the hexagonal omega (C32) structure. To reproduce its bulk electronic structure, a slab cluster, illustrated in Fig. 1, is embedded in the Madelung potential (MP), which is to be evaluated self-consistently in terms of charge transfer from Mg to B. Numerical atomic orbitals obtained in the crystal field are used as basis

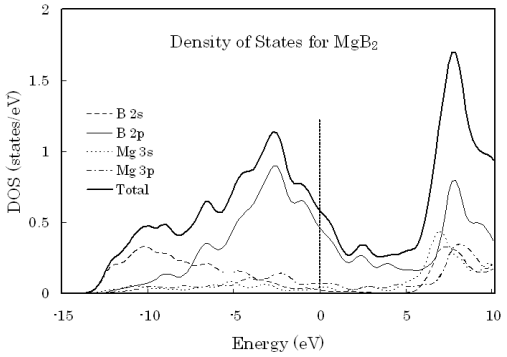

Fig. 2. Total and partial density of states for MgB_2 ($a = 3.084$, $c = 3.522$).

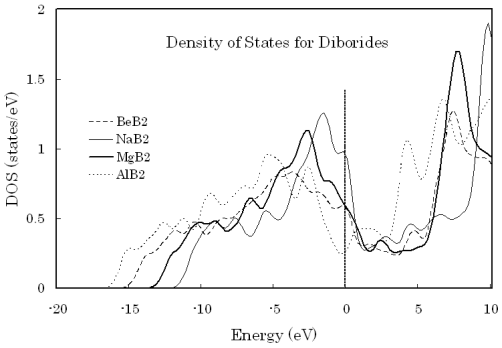

Fig. 3. Density of states for BeB_2 ($a = 2.87$, $c = 2.85$), NaB_2 ($a = 3.02$, $c = 4.19$), MgB_2 and AlB_2 ($a = 3.009$, $c = 3.262$).

functions. Unlike the band calculations, the periodicity of crystal lattices is not essential for this approach.

3. Results and Discussion

Figure 2 shows the total and partial density of states (DOS) for MgB_2. The states around the Fermi level E_F are dominantly derived from B $2p$ orbitals; thus, the B $2p_{x,y}$ electrons contribute both to the in-plane B-B bonding and to two-dimensional superconductivity. In Fig. 3, the DOS curves of BeB_2, NaB_2, MgB_2 and AlB_2 are compared, where the converged negative charge of B are 0.32, 0.16, 0.39 and 0.52, respectively. Except for AlB_2 with completely filled σ bands, the overall shapes are quite similar. The relatively small values of the charge transfers compared to the simple ionic picture indicate that the transferred electrons are not well localized at the B sites.

In the framework of Mulliken's population analysis, bond overlap population is a good measure of the *covalency* of the bonds. The calculated values of neighboring B-B (Mg-B) bonds are 0.76 (0.12), 0.74 (0.13), 0.70 (0.20) and 0.66 (0.28) for BeB_2, NaB_2, MgB_2 and AlB_2, respectively. The existence of σ holes can be understood from the overlap population diagram for the neighboring B-B bonds of MgB_2 shown in Fig. 4. The bonding component of the overlap population extends over E_F. The results for BeB_2 and NaB_2 are also similar, apart from their σ band broadening.

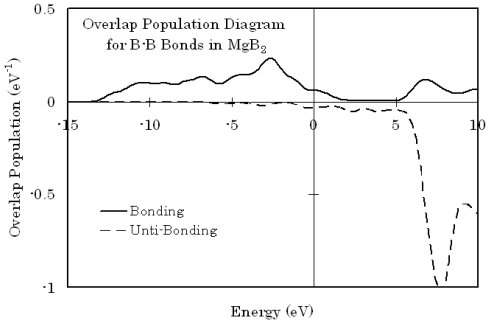

Fig. 4. Overlap population diagram for the neighboring B-B bonds in the B planes of MgB_2.

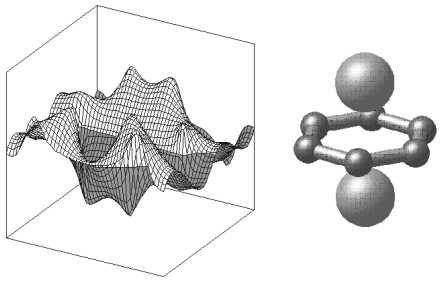

Fig. 5. Wave function at E_F in the B planes of MgB_2.

The wave function at E_F (see Fig. 5) consists of dominantly B $2p_{x,y}$ orbitals in the B planes of MgB_2. Its slightly asymmetric form suggests that the corresponding $\boldsymbol{k}$ lies in the vicinity of the Γ point in the Brillouin zone. As for AlB_2, these $2p_{x,y}$ orbitals are completely filled and do not contribute to conduction.

In the process of iteration, we have found that depending on the MP, the relative location of the σ and π bands shifts on the energy scale; accordingly, the hole doping in the B planes is sensitive to the MP along c axis. We expect that higher T_c could be achieved in artificially layered systems with modified MP.

References

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu, Nature **410** (2001) 63.

[2] J. Kortus, I.I. Mazin, K.D. Belashchenko, V.P. Antropov, L.L. Boyer, Phys. Rev. Lett **86** (2001) 4656.

[3] H. Adachi, M. Tsukada, C. Satoko, J. Phys. Soc. Jpn. **45** (1978) 875.