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Electronic structure of barium hexaboride

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Abstract. The electronic structure and the Fermi surface BaB_6 are studied as a function of doping in a conventional bandstructure approach based on the local density approximation to density functional theory (LDA). In particular it is shown that magnetic breakthrough can occur between the two sheets of the Fermi surface disconnected by electron-hole mixing and the spin-orbit interaction. It is further suggested that angle-resolved photoemission will see a single ellipse in the (100) plane for certain doping values, due to the finite energy/momentum resolution of the method. Transport properties, computed within Bloch-Boltzmann theory, are also presented. The bare plasma energy is found to be ≈ 0.6 eV in the stoichiometric compound.

PACS. 71.28.+d Narrow-band systems; intermediate-valence solids – 71.20.-b Electron density of states and band structure of crystalline solids

1 Introduction

The alkaline earth hexaborides were long thought to be simple polar semiconductors with single-particle gap energies of several tenths of an eV [1–3]. The first quantitative calculation on CaB_6 [4], however, suggested the existence of a small overlap between a boron-derived valence band and a metal-derived d-band near the X point of the simple cubic Brillouin zone, rendering the compound semimetallic. The authors of that paper also pointed out the extreme sensitivity of the bandstructure in the vicinity of the Fermi level E_F to the details of the crystal geometry. More recent LDA treatments of CaB_6 [5,6] and SrB_6 [5,7] have confirmed their picture. In particular it was found that a change of only two percent in the internal coordinate x describing the distance of a boron atom to the closest pure metal plane (see Fig. 1), is enough to transform the overlap into a gap in SrB_6 [5].

The subtlety of the electronic structure of these compounds is further borne out by experiment, in the form of a very strong dependence of their physical properties on stoichiometry or doping, culminating in the observation of ferromagnetism with a small moment and a high Curie temperature in $Ca_{1-x}La_xB_6$, $Sr_{1-x}La_xB_6$, $Ca_{1-x}Th_xB_6$, $Ca_{1-x}Ba_xB_6$ in a narrow range of concentrations [8], and even in nominally pure CaB_6 [9] and SrB_6 [10]. In the latter two systems, the magnetism is attributed to the presence of vacancies on the metal sublattice, leading to hole doping, and indeed vanishes in crystals grown from a flux containing an excess of alkaline earth atoms. The vanishing of the magnetization is accompanied by an increase of the resistivity below 100 K by four orders of magnitude [9], towards values typical for a lightly doped semiconductor. If the extra metal ions truly fill the cation vacancies, the above finding suggests that the stoichiometric alkaline earth hexaborides have a gap in their low energy excitation spectrum.

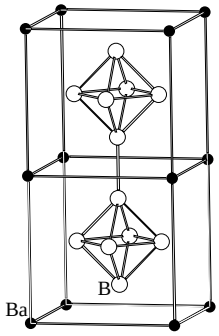

Fig. 1. Crystallographic structure of barium hexaboride. The Ba atom is at the origin of the cubic unit cell, while the B atoms are at $(\frac{1}{2},\frac{1}{2},x)$, $(\frac{1}{2},\frac{1}{2},1-x)$, $(\frac{1}{2},x,\frac{1}{2})$, $(\frac{1}{2},1-x,\frac{1}{2})$, $(x,\frac{1}{2},\frac{1}{2})$, $(1-x,\frac{1}{2},\frac{1}{2})$.

The existence of such a gap, attributed to the formation of an excitonic condensate, has been postulated by Zhitomirsky *et al.* [6] in their theory of the ferromagnetism in these compounds, which is consistent with all the observed features. A qualitative criterion for the stability of this new insulating phase relative to the semimetallic state predicted by the band structure calculation is that, in the latter, the overlap between the valence and the conduction band has to be of the same order of magnitude

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or smaller than the excitonic Rydberg $E_x = m_{\rm opt}\varepsilon_\infty^{-2}$ Ry, where $m_{\rm opt}$ is the optical mass in units of the free electron mass [11,12]. The LDA produces overlaps which are slightly larger than the values obtained for E_x from the corresponding band masses and experimental estimates for ε_∞, so that no clear cut conclusion can be reached yet as to the occurrence of the excitonic condensate in these systems.

Very recently, Rodriguez *et al.* [7] have recalculated the band structure of SrB_6 in great detail, and they argue on the basis of a comparison of their results with the available experimental data [13,14] that this compound is well described by band theory down to at least 5 K. The samples used in reference [13] were grown without special precautions to make them stoichiometric and also show ferromagnetism [10]. It is therefore very likely that they are hole doped, due to the presence of Sr vacancies. According to the phase diagram drawn by Zhitomirsky *et al.* [6] for $Ca_{1-x}La_xB_6$, even if the excitonic condensate represents the true ground state at stoichiometry, a vacancy concentration of the order of 1% may be sufficient to restore a conventional Fermi liquid behaviour. This, together with the fact that Fermi surface cross-sections have actually been observed in SrB_6 by angle-resolved photoemission [15] and in CaB_6 and SrB_6 by de Haas van Alphen experiments [14] makes it worthwhile to investigate the electronic structure of these systems and in particular the dependence of the Fermi surface on $E_{\rm F}$ more carefully by standard band structure methods.

In the following we present such results for BaB_6. Due to the relatively high atomic number of Ba, the spin-orbit (SO) interaction, negligible from a practical point of view in CaB_6 and SrB_6, now induces small gaps between the valence and conduction band, which were allowed to cross on the high symmetry planes of the BZ in a semirelativistic treatment. We study the change of the Fermi surface (FS) topology as the Fermi level is moved into these gapped regions by doping.

2 Computational details

Our electronic structure calculations are performed using the all-electron full-potential linearized augmented plane wave (FLAPW) [16] method, within the local density approximation (LDA) for exchange and correlation, as parametrized by Hedin and Lundqvist [17]. In our scheme the core states are calculated fully relativistically and updated at each iteration, whereas for the valence states, which include the Ba 5*p*–orbitals, a selfconsistent semirelativistic calculation is performed, after which the SO coupling is introduced as a perturbation.

Inside the muffin-tin spheres, the wave function is expanded in spherical harmonics up to $l_{\rm max} = 8$, while $l_{\rm max} = 6$ is used for the charge density and the potential expansions. In order to calculate the Fermi level accurately, integrations over the irreducible wedge of the Brillouin zone (BZ) are performed using 60 **k**-points within the linear tetrahedron method [18]. To fine-tune the value of $E_{\rm F}$ the number of independent **k**-points is increased to 2 600, and a spline fit of the corresponding energies is performed [19]. The fitted energies over $\approx 44\,000$ independent **k**-points are then used to obtain the density of states close to $E_{\rm F}$. The muffin-tin radii used are 3 a.u. for Ba and 1.55 a.u. for B. Convergence is achieved with a plane wave cutoff $K_{\rm max} = 4.1$ a.u.

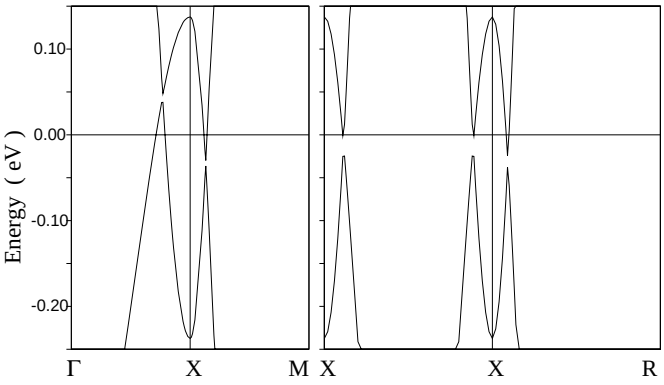

Fig. 2. Electronic band structure for BaB_6. All gaps are due to the spin-orbit interaction. The line X-X connects the centers of two adjacent faces of the BZ.

3 Results

The minimization of the semirelativistic energy functional leads to an equilibrium lattice constant $a = 4.343$ Å and to the value $x = 0.207$ for the internal coordinate, compared to the experimental results $a = 4.2706$ Å and $x = 0.205$, respectively [20]. At the level of accuracy at which they are quoted, the theoretical values for the structural parameters will not be affected by the SO interaction, given the low number of *d*-electrons involved and the small value of the SO splitting. The effect of the latter on the bandstructure can be seen in Figure 2. The density of states (DOS) obtained by the procedure outlined in the preceding section is shown in the upper panel of Figure 3. At this point, a word of caution seems appropriate. The tetrahedron method, even in its most sophisticated form [21], is known to be inaccurate near band crossings, as it interpolates the functions $\epsilon_n(\mathbf{k})$ within bands numbered in increasing order of energies and thereby transforms crossings into anticrossings, which leads to spurious peaks in the DOS. The problem can be reduced by making the tetrahedra smaller. This however requires a finer mesh of **k**-points over which the energies have to be known. For economical reasons, the values at the extra **k**-points are in general obtained through a global interpolation procedure using a symmetrized Fourier expansion over direct lattice vectors, whose coefficients are fitted to the *ab initio* results on a considerably smaller subset (here 2 600 *vs.* 44 000). We have found that, even with 9 000 R-stars, the fitted bands differ by $\approx 1{-}2$ mRy from the first principles ones near the crossing points, so that one problem has been replaced by another. In the lower panel of Figure 3, we also show the results obtained by approximating the band structure in the overlap region by two anisotropic

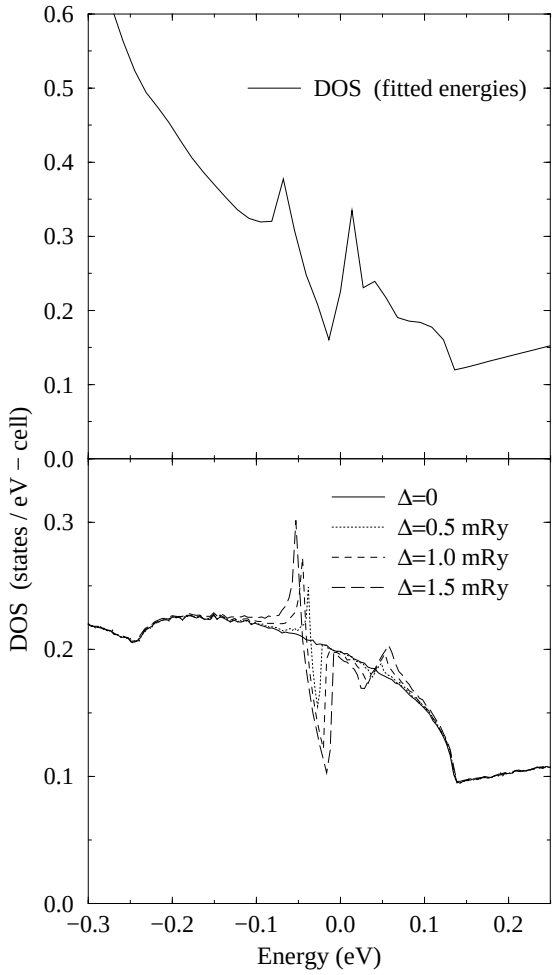

Fig. 3. Density of states for BaB_6 obtained from the interpolated *ab initio* band structure (upper panel). Model densities of states for two overlapping anisotropic parabolic bands coupled by a **k**-independent matrix element Δ (lower panel).

parabolic bands with the effective masses at the X-point equal to (in units of the free electron mass) $m_{\rm h}^{\parallel} = -1.095$, $m_{\rm h}^{\perp} = -0.191$, $m_{\rm e}^{\parallel} = 0.362$, $m_{\rm e}^{\perp} = 0.154$, coupled by a **k**-independent matrix element Δ. The curve for $\Delta = 1$ mRy should give an upper limit to the spikiness induced by the hybridization and the spin-orbit interaction. For energies outside of the overlap region, the difference between the model calculation and the *ab initio* one reflects the non parabolicity of the LDA bands as one moves away from the X-point. In any case, the low value of the DOS in the region around $E_{\rm F}$ implies a strong dependence of the chemical potential on carrier concentration in a rigidband picture: a one percent doping with electrons (holes) leads to a positive (negative) shift of the Fermi level by $\approx +3$ (≈ -4) mRy . To illustrate the sensitivity of the FS to doping, we show cuts in the (001) plane through X, in the (010) plane through Γ and in the (110) plane through Γ in Figures 4a–4c, respectively, taken at the LDA Fermi energy and at 1 mRy above it. While Figure 4a suggests that the FS is cylindrically symmetric around the Γ-X

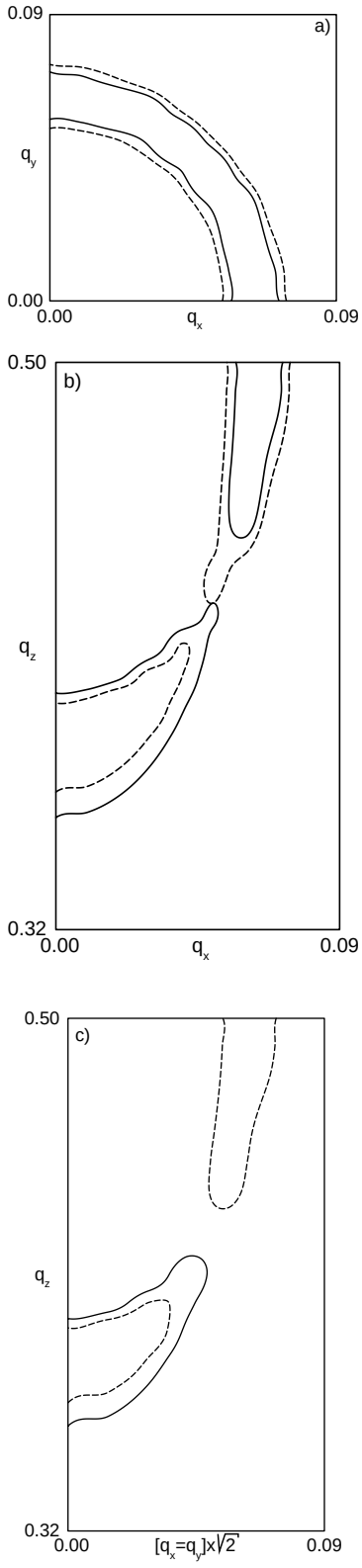

Fig. 4. Cuts through constant energy surfaces for BaB_6, at the LDA Fermi energy (continuous line) and 1mRy above it (dashed line); (a) (001) plane through X; (b) (010) plane through Γ; (c) (110) plane through Γ. The units of the axes are $2\pi/a$, with $a = 4.343$ Å.

Table 1. Extremal areas F (in tesla) and cyclotron masses m_c (in units of the free electron mass) on the Fermi surface of BaB_6. See the text and Figure 4 for the labeling of the orbits.

	$O_{a),e}$	$O_{a),h}$	$O_{b),e}$	$O_{b),h}$	$O_{c),e}$	$O_{c),h}$
F	346	227	28	71	≈ 0	66
m_c	$+0.23$	-0.20	$+0.15$	-0.27	–	-0.24

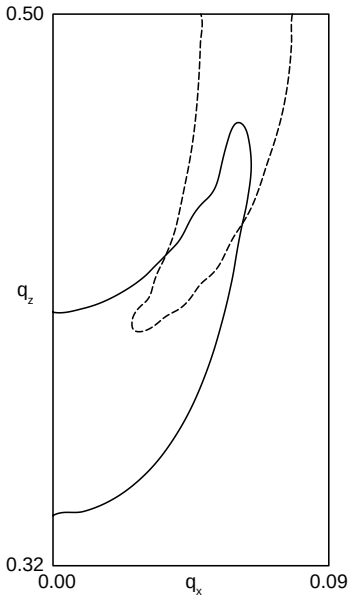

Fig. 5. Cut through the constant energy surface at 2.5 mRy below (continuous line) and 3 mRy above (dashed line) the LDA Fermi energy in a (100) plane through Γ for BaB_6. The units of the axes are $2\pi/a$, with $a = 4.343$ Å.

axis, a comparison of the cuts in the other two planes shows that the symmetry is only D_{4h}. In particular, the electron sheet at E_F, which is clearly visible in the (010) plane, is to small to be resolved within our accuracy in the (110) plane, although it is expected to be there according to Figure 4a. The areas F and cyclotron masses m_c for the corresponding extremal orbits at E_F, labelled by the figure in which they appear, and by e for electrons and h for holes, are listed in Table 1. Note that without the SO interaction, the electron and hole sheets would touch each other at a cusp in the symmetry planes of Figures 4b and 4c [4]. Moving the Fermi level by -2.5 mRy into the lower spin-orbit gap, which corresponds to a doping with 0.7% holes, leads to a single FS sheet, whose cut with the (010) plane through Γ is shown as a continuous line in Figure 5 and has a total area of 169 teslas (T). A further lowering of E_F by as little as 0.2 mRy, will make this sheet intersect with the (001) face of the BZ at points outside the symmetry planes containing the Γ-X axis. On the other hand, a shift of the Fermi level by $+3$ mRy produces a single, electron-like FS sheet, whose cross section is appears as a dashed line in Figure 5, and has an area of 106 T.

In all examples shown, the underlying elliptic cross sections which would be seen in the absence of mixing between the valence and conduction band are clearly apparent, and the question arises, whether magnetic breakthrough could reestablish these orbits. The condition for this to happen is:

$$\frac{\hbar\omega_c \epsilon_F}{E_{gap}^2} > 1, \tag{1}$$

where $\hbar\omega_c$ is equal to $8.53 \times 10^{-3} \times (m_{free}/m_c)$ mRy/T, and ϵ_F is the Fermi energy measured from the bottom of the band, in the absence of the perturbation leading to the splitting of the FS-sheets, which can be read from Figure 2 to be 9 mRy for the hole band and 19 mRy for the electron band. E_{gap}, the energy difference between the two bands at the points where the transition would take place, is typically one to two mRy, so that, with our values for the cyclotron masses, magnetic breakthrough orbits should be observable in fields above ≈ 12 T. The corresponding areas at the LDA Fermi level are ≈ 518 T and ≈ 564 T for electrons and holes, with approximate axis ratios $518/369 \approx 1.5$ and $564/227 \approx 2.5$, respectively. A situation similar to the one just described for the breakthrough orbits is expected to occur in angle-resolved photoemission spectroscopy. Due to the finite energy/momentum resolution of the method and if, for some range of doping, the FS of the real system is close to the one illustrated in Figure 4, the experiment will see its (010) cross section as one single large elliptic curve, with an increased thickness accompanied by an intensity modulation near the Γ-X axis.

From our knowledge of the FS as a function of E_F we can deduce the doping dependence of the conduction properties of BaB_6 within a rigid band picture, using Bloch-Boltzmann theory [22]. As seen in Figure 6, the LDA yields a minimum of the bare plasma energy $\Omega_p \approx 0.6$ eV, near zero doping. Due to the mixing between the valence and conduction band, the Hall constant has a resonance-like shape as a function of E_F. Outside of the overlap region it takes the free-electron behaviour $1/ne$.

4 Discussion

We have presented detailed predictions for the electronic structure, Fermi surface and conduction properties of BaB_6 as a function of doping, in a rigid band picture. These were obtained within the LDA for exchange and correlation; more sophisticated functionals will lead to smaller sizes of the band overlap, which may yet take a third, different value in the true quasiparticle spectrum.Therefore, our results have to be considered as qualitative, the most important message (besides the caveat on the DOS calculation) being the extreme sensitivity of the FS to doping.

We have not addressed the question of the potential ferromagnetism in these system, as it lies beyond the capabilities of our method. The existence of an excitonic gap at perfect stoichiometry also remains open. From our band

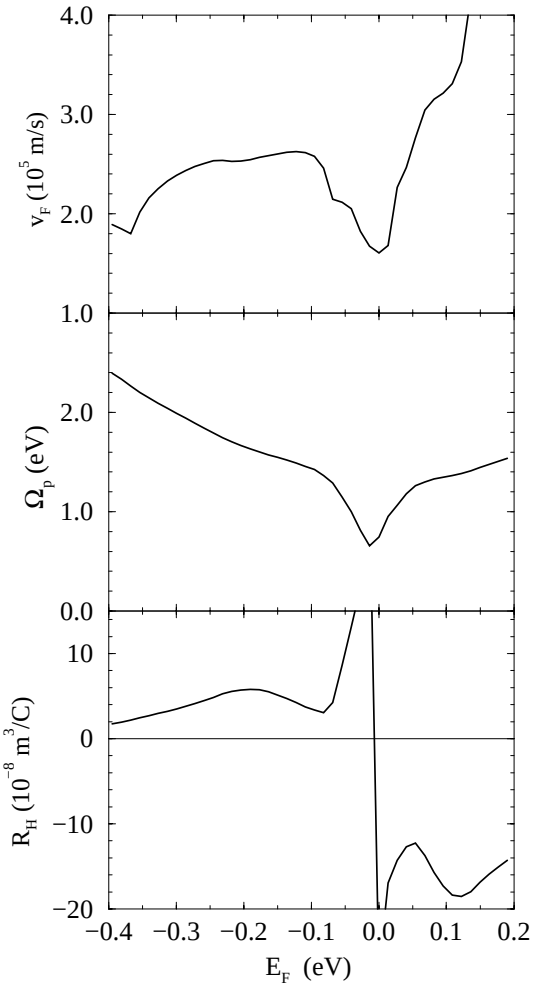

Fig. 6. Conduction properties of BaB_6 as a function of doping in a rigid band picture. $E_F = 0$ corresponds to the LDA Fermi energy of the undoped, stoichiometric compound. The doping range considered is from 0.25 holes to 0.04 electrons per formula unit.

structure, we deduce a value of $\approx 0.1 m_{\text{free}}$ for the optical mass at the X point, and we expect ε_∞ to be of the same order of magnitude as in the lighter alkaline earth hexaborides, which puts the excitonic Rydberg E_x at about 0.06 eV. This is comparable to the overlap of the bands between the two spin-orbit gaps, but considerably smaller than the the overlap at the X point. As mentioned above, even without considering electron-hole pairing, manybody effects beyond those contained in the LDA will reduce the overlap, and therefore favour the formation of the excitonic phase. On the other hand, the interaction of the charge carriers with the optical phonons, not considered in this work, will increase both the optical mass and the dielectric constant, the net effect being to lower the value of E_x; at the same time, the bottom of the bands involved will be shifted to lower energy (that is, upwards in Fig. 2 for the hole band). Altogether, this means that, if in the rigid crystal the bands overlap, the electron-phonon interaction will inhibit the formation of the excitonic condensate. If, however, the valence and conduction bands are separated by a gap, it may favour it. We hope that transport experiments on carefully prepared samples will soon answer this exciting question.

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