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The loss of anisotropy in MgB₂ with Sc substitution and its relation with the critical temperature

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Abstract

The electrical conductivity anisotropy of the σ -bands is calculated for the (Mg, Sc)B₂ system using a virtual crystal model. Our results reveal that the anisotropy drops with relatively little scandium content (<30%); this behaviour coincides with the lowering of T_c and the reduction of the Kohn anomaly. This anisotropy loss is also found in the Al and C doped systems. In this work it is argued that the anisotropy, or 2D-character, of the σ -bands is an important parameter for the understanding of the high T_c found in MgB₂.

1. Introduction

Shortly after the discovery of 40 K superconductivity in MgB₂, the electronic nature of this system and its relation with the superconductivity was intensively studied (Kortus *et al* 2001 and Physica C 2003). MgB₂ is a many-band superconductor, with two bi-dimensional (2D) σ -bands and two three-dimensional (3D) π -bands at the Fermi energy. The dominant contribution to the superconductivity comes from the σ -bands (Canfield and Crabtree 2003). When magnesium is substituted by aluminium or boron is substituted by carbon, the σ -levels start to fill up and T_c diminishes and disappears when there are no more available σ -levels. de la Peña *et al* (2002) showed that in the aluminium doped system T_c is proportional to the number of σ -carriers; recently Kortus *et al* (2005) argued that aluminium and carbon doping can be understood in terms of band-filling and interband scattering, while de la Mora *et al* (2005) found that such proportionality is clearly related to the in-plane σ -electrical conductivity.

Magnesium, in MgB₂, has also been experimentally substituted by scandium to form the superconducting ternary system (Mg_{1-x}Sc_x)B₂ (Agrestini *et al* 2004a, 2004b), for $0 < x < 0.27$. The fully doped compound ScB₂ has a low T_c (~ 1.5 K) (Samsonov and Vinitsky 1976). Electronic structure results show several different effects of Mg substitution by Sc in MgB₂; among these effects there are two that should be remarked upon. First, there are large changes in the morphology of the σ -bands, suggesting a change of dimensionality

of the electronic process. Second, E_F increases and comes close to the σ -band edge, but does not go above it; as a consequence the σ -band conductivity in the a -direction, σ_a^σ , reduces but does not disappear, as is the case in $(\text{Mg}, \text{Al})\text{B}_2$ and $\text{Mg}(\text{B}, \text{C})_2$. Calculations show that the ScB_2 σ -band anisotropy, $\sigma_a^\sigma/\sigma_c^\sigma = 3.9$, is much lower than for MgB_2 ($=43$) (de la Mora *et al* 2005). On the other hand, in $(\text{Mg}_{1-x}\text{Sc}_x)\text{B}_2$, the experimental results show that T_c is already as low as 6.2 K at $x = 0.27$. These comparative results reveal that the T_c drop cannot be explained by the reduction of σ -band carriers alone, as is the case for $(\text{Mg}, \text{Al})\text{B}_2$ and $\text{Mg}(\text{B}, \text{C})_2$ (as discussed by Kortus *et al* 2005), but a large reduction of the σ -band anisotropy seems to play an important role in this system.

As suggested by the chemical composition of the system $(\text{Mg}, \text{Sc})\text{B}_2$, initially the method of supercells was tried for band structure calculations, but it was found to be inappropriate since it changes the band anisotropies more than it should and also mixes the σ - and π -bands, so that the pure σ -band contribution can no longer be extracted. An alternative model for MgB_2 was designed by replacing Mg by a (K, Ca) virtual atom with a nuclear charge of 19.4. Starting from this situation the solid solution with Sc can be done with the approximation of the virtual atom (virtual crystal approximation). This methodology has been selected in order to preserve the scenario in which it is possible to analyse separately the topological nature of the σ - and π -bands in one system. This is crucial, since the T_c value seems to be closely related to the σ -band anisotropy. Within the virtual crystal approximation it was found that even with a small scandium substitution the σ -band anisotropy diminishes rapidly, then at $x \sim 0.3$ it levels off and continues to diminish but at a much lower rate. The rapid anisotropy diminution coincides with the experimental drop of T_c , revealing that the anisotropy of the σ -bands is an essential characteristic of the high T_c value in MgB_2 . In other words, our calculations show that when the σ -bands lose their two-dimensional character the compound becomes a low T_c superconductor.

2. Computational procedure

The electronic structure calculations were done using the *WIEN2k* code (Blaha *et al* 2001), which is a full potential linearized augmented plane wave (FP-LAPW) method based on DFT. The generalized gradient approximation of Perdew *et al* (1996) was used for the treatment of the exchange–correlation interactions. The energy threshold to separate localized and non-localized electronic states was -6 Ryd. For the number of plane waves the criterion used was $R_{\text{MT}}^{\text{min}}$ (muffin tin radius) $\times K_{\text{max}}$ (for the plane waves) = 9. The number of k -points used, for single-cell calculations, was $19 \times 19 \times 15$ (320 in the irreducible wedge of the Brillouin zone). The muffin-tin radius was chosen $1.8 a_0$ for magnesium and $1.53 a_0$ for boron (a_0 is the Bohr radius). The charge density criterion with a threshold of 10^{-4} was used for the convergence. A denser mesh of $100 \times 100 \times 76$ (34 476 in the irreducible wedge) was used for the evaluation of the electrical conductivity. For the case of the MgScB_2 supercell only half of the k -points were used due to reciprocal-cell reduction.

3. Band anisotropy

3.1. Theory

The electrical conductivity was calculated, within the relaxation time approximation and at $T = 0$, as in de la Mora *et al* and references within (de la Mora *et al* 2005).

$$\sigma_\alpha^\beta = \frac{e^2 \tau^\beta}{\hbar \Omega_0} \int dA_\alpha \sum_i |v_\alpha^{i\beta}(k_F)| \quad (1)$$

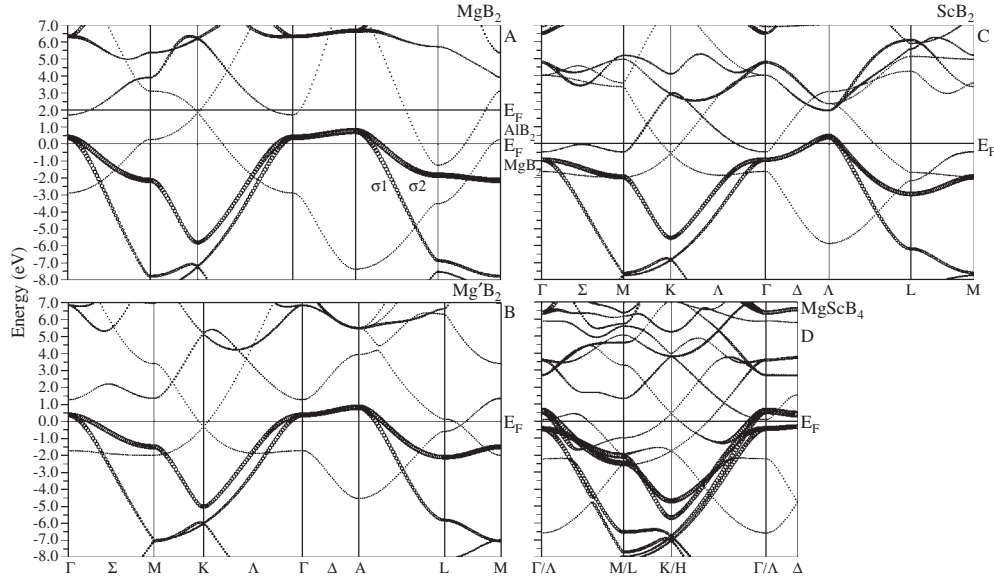


Figure 1. Band structure of (A) MgB₂: the thick lines correspond to the σ -bands. AlB₂ has a quite similar band structure, but with E_F at approximately 2 eV above; (B) Mg'B₂ adjusted model (see text): the σ -bands are quite similar to MgB₂; (C) ScB₂: E_F is higher than in MgB₂, but not above the σ -bands; also the σ -band slope in the c -direction (Γ -A, L-M) is considerably higher; and (D) MgScB₄ calculated with the supercell model: the symmetry labels correspond to the single cell labels so that it can be compared with other band structures. Note the splitting that appears in the σ -bands at Δ .

where β is the band index, τ is the relaxation time, Ω_0 is the reciprocal-cell volume, A_α is the area perpendicular to the α -direction, $v_\alpha^{i\beta}$ is the electron velocity in the α -direction and can be calculated as the slope of the β -band ($=\hbar^{-1}\partial\varepsilon^\beta/\partial k_\alpha$), $v_\alpha^{i\beta}(k_F)$ is evaluated at E_F , and the sum over i is for all the crossings of the β -band at E_F . From this equation the band anisotropies can be evaluated with $\sigma_a^\beta/\sigma_c^\beta$.

The band anisotropy can approximately be analysed with the expression (de la Mora *et al* 2005)

$$\frac{\sigma_a^\beta}{\sigma_c^\beta} \approx \frac{v_a^2}{v_c^2} \approx \frac{A_a^2}{A_c^2}. \quad (2)$$

The relation between conductivities, $\sigma_a^\beta/\sigma_c^\beta$, and areas, A_a^2/A_c^2 , was found to be correct within 17% for the (Mg, Al)B₂ system.

3.2. Discussion

The objective of this paper is to study theoretically the effect on the σ -band anisotropy, $\sigma_a^\sigma/\sigma_c^\sigma$ (σ_a^β is the conductivity of the β -band in the α -direction and should not be confused with σ , which is used to refer to the symmetry of bands), of the scandium substitution on MgB₂, and how this anisotropy can be related to the experimental reduction of T_c .

The band structure of MgB₂ and ScB₂ can be seen in figures 1(A) and (C); the thick lines near the Fermi energy (E_F) are the σ -bands, $\sigma 1$ being the lower one and $\sigma 2$ the upper one. There are two other bands, the π -bands, with thin lines.

Observing the band structure of MgB_2 it can be seen that in the a - b plane (Γ -M-K- Γ and A-L) the σ -bands have a large slope; in contrast, in the c -direction (Γ -A and L-M) they have a small slope. Therefore these bands can be expected, from expression (2), to be highly anisotropic; the calculated value for $\sigma_a^\sigma/\sigma_c^\sigma$, using equation (1), was 43.

AlB_2 has a very similar band structure to MgB_2 . Aluminium $[\text{Ne}]3s^23p^1$ contributes with one electron more than magnesium $[\text{Ne}]3s^2$ and thus E_F is about 2 eV higher, which is above the σ -bands, and thus these bands no longer contribute to the conductivity; AlB_2 is not a superconductor, which is consistent with the observation that the σ -bands are the responsible for the high T_c in MgB_2 . The most prominent difference, besides the E_F shift, is a lowering of the π -bands relative to the σ -bands. Due to the similarity of the band structure of these compounds, the rigid band approximation can be applied very well for the computation of σ_a^σ in the (Mg, Al) B_2 system (de la Mora *et al* 2005).

Scandium $[\text{Ar}]4s^23d^1$ in ScB_2 also has one valence electron more than magnesium, but in contrast to aluminium with a 3p orbital, the scandium adds a 3d orbital with a different symmetry. The latter is crucial when the orbitals hybridize with the boron σ -orbitals reducing their 2D-character. The corresponding electronic structure is quite different to AlB_2 (figure 1(C)); E_F is still within the σ -bands but, in comparison with MgB_2 , it has a much larger slope in the c -direction and smaller in the a - b direction; see for example σ_2 in the Γ -M section. Correspondingly, the respective σ -band anisotropy is much lower, namely 3.9.

For the (Mg, Al) B_2 and $\text{Mg}(\text{B}, \text{C})_2$ systems the T_c reduction with doping has been explained as a consequence of the reduction of the σ -band carriers (de la Peña *et al* 2002, Kortus *et al* 2005, de la Mora *et al* 2005). In the (Mg, Sc) B_2 system the drop of T_c cannot be completely related to the reduction of σ -band carriers since with 27% of scandium substitution the system has a low T_c (~ 6 K) (Agrestini *et al* 2004a, 2004b), and even in ScB_2 the system has quite a few σ -band carriers ($\sigma_a^\sigma(\text{ScB}_2) = 0.12\sigma_a^\sigma(\text{MgB}_2)$). On the other hand, the anisotropy is reduced from 43 in MgB_2 to 3.9 in ScB_2 . Therefore the T_c reduction cannot be entirely ascribed to the reduction in σ -band carriers but it should also be associated to the loss of σ -band anisotropy. The 2D character of the σ -bands should be considered as an important feature of the high T_c in MgB_2 .

4. Model

The $(\text{Mg}_{1-x}\text{Sc}_x)\text{B}_2$ solid solution has been obtained experimentally in the AlB_2 structure for $x = [0-0.02]$ and $[0.12-0.27]$ (Agrestini *et al* 2004b). The electronic structure calculation for this solid solution presents several difficulties. One method that could be used is based in constructing supercells; it consists in repeating the unit cell n times, replacing magnesium by scandium in m of them. We found three problems with this method;

- (A) When the unit cell is repeated in the a - b plane the calculations show that the σ - and π -bands hybridize and mix, therefore there are no longer pure σ - or π -bands. In this case the properties, such as the conductivity, of the pure σ -bands cannot be directly extracted; instead these properties would have a mixed σ - or π -character. In this paper we are interested in the pure character of the σ -bands since they are the responsible for the high T_c in MgB_2 (Canfield and Crabtree 2003, de la Peña *et al* 2002, Kortus *et al* 2005).
- (B) In the supercell model magnesium and scandium would have a crystalline order, that is, they are not disordered as in the real compound. As a consequence, certain directions may be favoured. For example, if the single unit cell is doubled in the c -direction to construct a supercell, one with Mg and the other with Sc, then the crystal would have alternating layers of magnesium and scandium. Magnesium and scandium produce a

different potential in the crystal, and thus the bidimensionality is enhanced; the σ -bands, that are already quite 2D, are split at Δ (figure 1(D)). This splitting reduces the slope of the bands in the c -direction and as a consequence σ_c^σ is reduced. In the π -bands, which are 3D, the splitting in Δ (at -4.7 eV) is minimal.

An extreme example would be a stack of three layers of MgB₂ followed by three layers of AlB₂. In this case AlB₂ does not have any σ -bands at E_F and σ_c^σ would be zero, but σ_a^σ would be different from zero. This would be seen in the band structure as a splitting at Δ and the bands in the c -direction would be completely flat.

- (C) By replacing Mg by Sc in m cells of the total n cells then $x = m/n$ is a fraction, that is, one cannot have a continuous sampling of x . In order to have a representative sampling for x , then n has to be large, which implies prohibitive computational costs.

An alternative method to surpass these problems is the virtual crystal approximation (VCA), in which the charge assigned to an atom is fractional instead of integer; this virtual atom has the mixed properties of the two contiguous atoms in the periodic table, one with nuclear charge n and the other with $n + 1$. This can be used for the (Mg_{1-x}Al_x)B₂ system (de la Peña *et al* 2002). In the VCA method Mg_{1-x}Al_x is replaced by a virtual atom M with a nuclear charge of $12 + x$ ($0 \leq x \leq 1$), resulting in the new system M^{12+x}B₂.

Mg and Sc have a large difference in nuclear charge; therefore, the VCA method cannot be directly applied to the (Mg_{1-x}Sc_x)B₂ system. On the other hand MgB₂ and CaB₂ should have similar properties, since Ca and Mg have the same number of valence electrons and they should be almost fully ionized in the compounds (as is the case of Mg in MgB₂, de la Mora *et al* 2002). With this similarity the (Ca, Sc)B₂ system could be used instead of the (Mg, Sc)B₂ system.

Calculations of CaB₂, however, showed that the σ -bands are not that similar to those of MgB₂, but are more between those of MgB₂ and ScB₂; in fact, the slope in the c -direction has increased. For this reason it was thought that instead of using calcium, a virtual K_{1-x}Ca_x atom could better represent magnesium. In order to simulate MgB₂, the system (K_{1-x}Ca_x)B₂ was studied with the VCA and with $x = 0.4$ the resulting band structure looks very similar to that of MgB₂. Further refinements were done on the cell parameters to adjust the bandwidths, both in the plane and in the c -directions. The adjusted cell parameters were $a = 3.0108$ Å and $c = 3.9742$ Å (in MgB₂ $a = 3.0864$ Å and $c = 3.5215$ Å). In the adjusted cell, but due to the reduced number of valence electrons, E_F was found to be lower than in MgB₂ and thus it was increased by $\Delta E_F = 0.04$ Ryd (0.54 eV).

The band structure of the fully adjusted cell is shown in figure 1(B). It can be seen that the σ -bands are quite similar to those of MgB₂, figure 1(A). On the other hand, the π -bands are quite different, but since we analyse the σ -bands, this difference should not influence the study of σ_a^σ , mainly since these bands are quite separated both in energy and in k -space at E_F . Our calculations show that the σ - and π -Fermi surfaces (FSs) are spatially well separated: the σ -FSs are around the Γ -A axis (the distance of the σ -FS to this axis is less than 0.44 of the Γ -K distance), while the π -FSs are near the vertical sides of the cell (the distance to the Γ -A axis is more than 0.80 of the Γ -K distance).

Since the π -orbitals are far from the σ -orbitals they act only as recipients of electrons in terms of the σ -conductivity, σ_a^σ . This effect has also been seen, but in a diminished way, in the (Mg_{1-x}Al_x)B₂ system (de la Mora *et al* 2005) where the π -bands shift downwards more than the σ -bands when x is increased, that is, the π -orbitals start to fill faster than the σ -orbitals and as a consequence σ_a^σ takes longer to vanish.

With this adjustment (K_{1-x}Ca_x)B₂, which will be referred to as Mg'B₂, can now be used as MgB₂, and the (Mg'_{1-x}Sc_x)B₂ solid solution can again be calculated with the VCA. The

cell parameters and ΔE_F for the intermediate values of x were linearly interpolated between the $\text{Mg}'\text{B}_2$ and ScB_2 values. In the solid solution $(\text{Mg}'_{1-x}\text{Sc}_x)\text{B}_2$, x is increased in intervals of $1/8$ from 0 to 1.

Within this framework, the results of σ_a^σ may not be very precise, but we hope to obtain reliable general trends of the σ -band behaviour as a consequence of the scandium doping.

5. Results and discussion

Observing the σ -bands in figure 1, it can be seen that $\sigma 2$ in MgB_2 (figure 1(A)) has a positive slope in $\Gamma \rightarrow \text{A}$ (above E_F) and in $\text{M} \rightarrow \text{L}$ (below E_F , both in the c -direction). On the other hand, in $\text{Mg}'\text{B}_2$ (figure 1(B)) the slope at $\text{M} \rightarrow \text{L}$ is negative; therefore at E_F the band slope (and also $\sigma_c^{\sigma 2}$) is very small. This is reflected in the corresponding FS, which is an almost straight tube and the band anisotropy obtained from expression (2) is very large (de la Mora *et al* 2005). On the other hand, $\sigma 1$ has the same slope in both band structures and this band should reproduce the correct behaviour of the anisotropy of the conductivity in $\text{Mg}'\text{B}_2$.

The σ -band conductivities for the model compound, $(\text{Mg}'_{1-x}\text{Sc}_x)\text{B}_2$, are shown in figure 2. σ_a^σ and σ_c^σ are shown in figure 2(A), while the anisotropy, $\sigma_a^\sigma/\sigma_c^\sigma$, is shown in figure 2(B).

As shown in figure 2(A), the in-plane conductivity, σ_a^σ , decreases continuously. On the other hand, the value of the c -direction conductivity, σ_c^σ , has a large increase at the beginning and then decreases. For the $\sigma 2$ -conductivity, $\sigma_c^{\sigma 2} \approx 0$ at $x \approx 0$, this is a consequence of the $\sigma 2$ -FS being an almost straight tube.

For $x = 0$ ($\text{Mg}'\text{B}_2$) $\sigma 1$ has an anisotropy of 67, which can be regarded in this model as close to the MgB_2 value of 43. For $\sigma 2$, due to the low value of $\sigma_c^{\sigma 2}$, the anisotropy is much higher, 1500, then it lowers quite rapidly, and for $x = 0.125$ it becomes 120. For low scandium content ($0 < x < 0.3$) both σ -band anisotropies drop rapidly to a low value, and at $x \approx 0.3$ they have the same value. After this interception they continue to drop, but at a much lower rate; in this range ($0.4 < x < 1$) they have almost the same value ($\sigma 1 \approx \sigma 2 \times 1.3$). The drop of T_c is in the range of low x , where there is a large anisotropy decrease ($0 < x < 0.3$). In this range the in-plane σ -conductivity has a moderate reduction of 35%. Therefore, the fall in T_c cannot be associated to the σ_a^σ diminution (which is related to the band-filling) as was the case of aluminium and carbon doped MgB_2 (de la Peña *et al* 2002, Kortus *et al* 2005, de la Mora *et al* 2005). The VCA treatment of the $(\text{Mg}'_{1-x}\text{Sc}_x)\text{B}_2$ system enhanced the anisotropy at $x \approx 0$ (67 in $\text{Mg}'\text{B}_2$ compared to the 43 in MgB_2); therefore in a more realistic model the value of the anisotropy at $x \approx 0.3$ should be lower. The anisotropy value, $\sigma_a^\sigma/\sigma_c^\sigma$, at $x = 0.27$ is ≈ 17 (figure 2(B)), which, if adjusted, could be as low as 11.

To further justify the $(\text{Mg}'_{1-x}\text{Sc}_x)\text{B}_2$ model, a supercell was made by piling MgB_2 and ScB_2 in the c -direction; for the a parameter the average value of the two cells was used, while for c the sum was used. Except for the substitutional order this cell would correspond to $(\text{Mg}_{0.5}\text{Sc}_{0.5})\text{B}_2$. This compound consists of alternating $\dots\text{B-Mg-B-Sc-B}\dots$ layers. Since scandium contributes less to the σ -conductivity than the material should have a smaller σ -conductivity in the c -direction, as explained above, and the anisotropy should be higher than that of a Mg-Sc disordered system.

The reciprocal cell of this $(\text{MgSc})\text{B}_4$ double cell is folded in half, so the $\Gamma\text{-M-K}$ and A-L-H planes of the single cell now fall into the $\Gamma\text{-M-K}$ plane of the double cell. Therefore the bands of both planes of the single cell can be seen in the $\Gamma\text{-M-K}$ plane, and the bands in the c -direction are cut in half and folded. In the band structure that is shown in figure 1d the $\Gamma\text{-M}$ and A-L bands are now in $\Gamma\text{-M}$, while the $\Gamma\text{-A}$ bands are folded; see for example the π -bands at -0.4 eV at Δ . In contrast, the σ -bands at E_F are split, due to the Mg-Sc layered arrangement, as mentioned above.

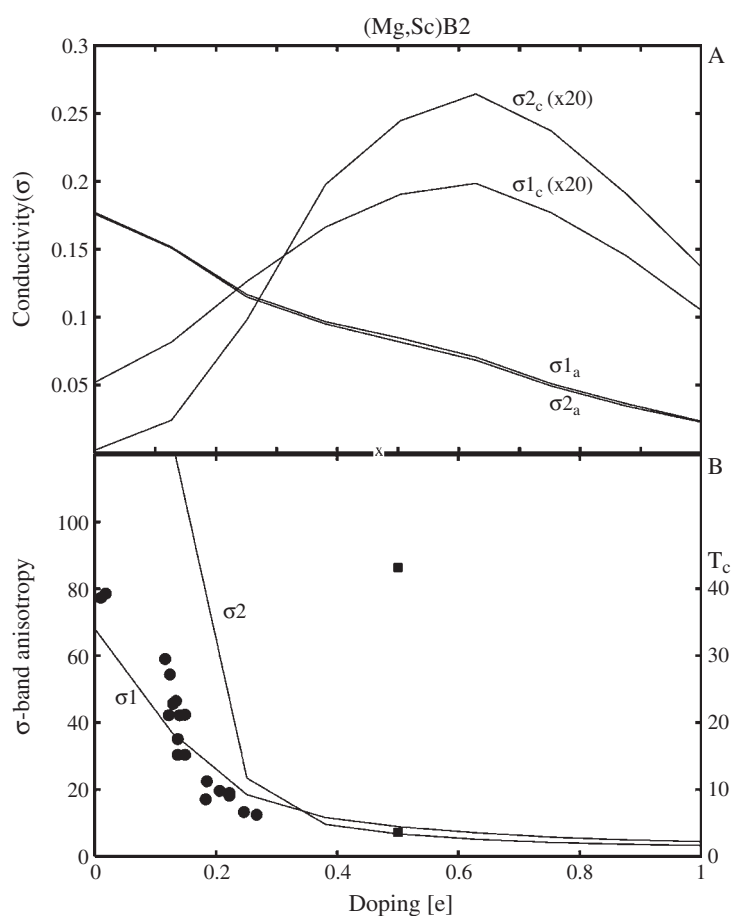


Figure 2. (A) σ -band conductivities (σ_1 , σ_2); σ_a^σ in the a - b plane and σ_c^σ in the c -direction (the c -component has been multiplied by 20), (B) σ -band anisotropies: the squares show the anisotropy of the MgScB₄ supercell, see text; the circles are the experimental values of T_c (Agrestini *et al* 2004b).

The value of the σ -band anisotropy for the (MgSc)B₄ supercell is 86, and is shown in figure 2(B) by the upper square. This large value is due to the large splitting in the σ -bands, seen at Δ of figure 1(D). This splitting quite considerably lowers the slope in the c -direction. In the real material magnesium and scandium should be randomly distributed and there should be no such splitting, as is the case for the π -bands. The σ -bands cross Γ at 0.5963 and -0.4448 eV and cross Δ at 0.4054 and -0.3358 eV; therefore the average slope would be 0.1500 eV/ δ , where δ is the Γ - A distance. If there would be no splitting at Δ the slope would increase to 0.5202 eV/ δ , that is, it would increase 3.47 times, and thus the conductivity, using expression (2), would increase by $3.47^2 = 12.03$ times. Therefore the anisotropy would lower from 86 to a value of 7.2. This is shown by the lower square in figure 2. This value fits the results of the (Mg_{1-x}Sc_x)B₂ model for $x = 1/2$ surprisingly well. Although this value cannot be taken as very precise, it shows that the VCA model is capable of reproducing some quantitative aspects of the (Mg_{1-x}Sc_x)B₂ system.

As an additional test to monitor the supercell methodology, a supercell was made by repeating the MgB₂ cell six times, three cells on the a - b plane and twice in the c -direction.

Then magnesium is replaced by scandium in one of the cells; the electronic structure of this cell shows that the σ - and π -bands get strongly mixed and can no longer be regarded as independent: these bands have both σ - and the π -character. The supercell method cannot be used to calculate σ -band anisotropies of $(\text{Mg}_{1-x}\text{Sc}_x)\text{B}_2$ for values of $x = 1/6, 1/3$, etc; the VCA model with the virtual magnesium Mg' seems to be the simplest suitable alternative.

Agrestini *et al* (2004a, 2004b) measured T_c as function of the scandium content in $(\text{Mg}_{1-x}\text{Sc}_x)\text{B}_2$; the values of the second paper are reproduced in figure 2(B) (the absence of values in the 0.02 and 0.12 range, is due to a miscibility gap). This coincides with the argument of Agrestini *et al* that the reduction of T_c can be associated to a 2D/3D electronic transition, although they call it an electronic topological transition (ETT). They associated this ETT to the point where the σ -FS tubes are split into elongated droplets and corresponds to the point when the E_F crosses the bands at the Γ -point (Bianconi *et al* 2002) (see for example the discussion in de la Peña *et al* 2002). They expected that the scandium concentration at the ETT to be $x = 0.12$. They also find a reduction of the Kohn anomaly going from MgB_2 to $(\text{Mg}_{0.8}\text{Sc}_{0.2})\text{B}_2$ (Agrestini *et al* 2004b); according to them ‘this can be understood if the Sc substitution has driven the chemical potential through the ETT, where the σ -FS has a 3D topology with a reduced Kohn anomaly’. It should be noted that for ScB_2 there is a further reduction of the Kohn anomaly. In other words, for $x = 0.12$ the Kohn anomaly has an intermediate value between those of MgB_2 and ScB_2 .

A reliable estimate of the dimensionality could result from the band anisotropy relation, $\sigma_a^\sigma/\sigma_c^\sigma$, which can be estimated from expression (2) by observing the areas span from the a - or c -directions. When the FSs of MgB_2 , corresponding to the σ -bands, are seen from the plane they are like tubes, but from the c -direction they are thin rings. At the ETT the anisotropy should be already quite small; therefore the material would have a 3D character. At $x = 0$ the σ -FS, observed from the c -direction, has a small area and the anisotropy is large; when the tubes become droplets, the ring, observed from above, now becomes a solid circle and the area is no longer small, that is, σ_c^σ is now large and the anisotropy becomes small. Therefore, there is an anisotropy reduction in the $0 < x < 0.35$ range. According to our calculations the ETT is not at $x = 0.12$ but at $x = 0.35$. It should be noted that this anisotropy change is smooth although it is large.

At this ETT we do not find any σ -band anisotropy jump, not even a sharp change of slope (this also applies to the case of aluminium substitution; see de la Mora *et al* 2005). This value does represent the point where the σ -band anisotropy curves have a smooth change in slope from a large one ($x < 0.35$) to a low one ($x > 0.35$). In this framework $x = 0.35$ represents the composition at which the σ -bands have reached a 3D character. According to our calculations, for $(\text{Mg}_{1-x}\text{Sc}_x)\text{B}_2$, a smooth and continuous 2D to 3D electronic dimensional transition (EDT) of the σ -bands is observed, but it is not related to the σ -FSs’ topological transformation (from tubes to droplets).

According to our electronic structure results of $(\text{Mg}, \text{Sc})\text{B}_2$ using the VCA, the EDT transition should be located in the region of $0.1 < x < 0.3$, which is also the region where a large reduction of T_c is found.

For $x = 0.2$ the σ 1-band anisotropy is ~ 15 – 23 , that can be seen as an intermediate 2D–3D value. Our studies of the band structure of $(\text{Mg}, \text{Sc})\text{B}_2$ based on the VCA can be used to reinterpret the results of Agrestini *et al* (2004b) for the Kohn anomaly: the σ -bands for MgB_2 are in the 2D regime whereas for the other extreme case of ScB_2 they are in the 3D regime. In this scenario $(\text{Mg}_{0.8}\text{Sc}_{0.2})\text{B}_2$ has an intermediate 2D–3D anisotropy value, which can be the reason for the intermediate value of the Kohn anomaly for this specific composition. In this way both the Kohn anomaly value and the σ 1-band anisotropy cannot be assigned to a definite 2D or 3D regime.

Table 1. Anisotropy values for the different systems at concentrations where T_c has reached low values.

System	$\sigma_a^\sigma / \sigma_c^\sigma$
(Mg _{0.73} Sc _{0.27})B ₂	11–17
(Mg _{0.5} Al _{0.5})B ₂	7.5
Mg(B _{0.85} C _{0.15}) ₂	13

Although T_c reduction in Al and C doping has been attributed to band-filling and interband scattering (de la Peña *et al* 2002, Kortus *et al* 2005, de la Mora *et al* 2005), anisotropy reduction must also play an essential role in these systems. With electronic structure calculations on (Mg, Al)B₂ and Mg(B, C)₂ within the VCA, we can also show that anisotropies in these systems drop to values comparable to those of the (Mg, Sc)B₂ system; at the doping values where the σ -bands become full, this doping corresponds to the lowest T_c in those systems. For the calculations the cell-parameter values of de la Peña *et al* (2002) for (Mg, Al)B₂ and those of Kazakov *et al* (2005) for Mg(B, C)₂ were used; these anisotropy values are shown in table 1.

The high T_c in MgB₂ is due to both the σ - and π -contributions, the former one being the strongest; scandium substitution, which mixes the σ - and π -bands (see figure 1(D)), tends to lower T_c, but without this mixing T_c would probably drop at a higher scandium content.

For the aluminium and carbon doped systems the reduction of T_c can be explained by band-filling, but in the case of scandium doping the band-filling is not complete; in fact, it is quite limited $\sim 35\%$. On the other hand, in the three systems the reduction of T_c is accompanied by a reduction of the anisotropy, that is, a 2D \rightarrow 3D change. Therefore the 2D character or the large σ -band anisotropy should be considered as responsible for the high T_c found in MgB₂.

6. Conclusions

The model presented here constitutes a phenomenological description based on the band anisotropy of the MgB₂ system. The VCA treatment, with the possibility of having independent contributions to the conductivity from the σ - and the π -bands, gives a plausible explanation of the high T_c behaviour in the (Mg, Sc)B₂ system.

In conclusion, a theoretical model to study the (Mg_{1-x}Sc_x)B₂ system is presented. With this model, based on the virtual crystal approximation, we are able to calculate the anisotropy of the electrical conductivity of the σ -bands. It is also shown that the calculation of this anisotropy is not possible with the method of supercells.

It has been shown that T_c reduction for the (Mg_{1-x}Sc_x)B₂ system cannot be explained by the reduction of σ -band carriers. In contrast, T_c and also the Kohn anomaly follows a quite similar tendency as the conductivity anisotropy of the σ -bands.

In the aluminium and carbon doped systems the T_c reduction has been explained by the reduction of σ -band carriers, but it should be noted that the loss of anisotropy is also present in these systems.

The σ -band anisotropy, or in other words, its 2D character, emerges as an essential factor in the superconductivity of MgB₂.

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