PHYSICAL REVIEW B **66**, 165114 (2002)

Polarized x-ray emission and absorption spectra of MgB_2

K. Kokko, V. Kulmala, and J. A. Leiro
Department of Physics, University of Turku, FIN-20014 Turku, Finland

(Received 3 March 2002; revised manuscript received 14 August 2002; published 30 October 2002)

The polarized *K*-emission and absorption spectra for MgB_2 have been calculated using the tight-binding linear muffin-tin orbitals method. Within the dipole approximation a strong anisotropy is found. The core-hole effect has also been included in the calculation of the absorption spectra shifting the empty *p*-like states of Mg significantly towards lower energies in comparison with those of the ground state calculation. For the *K*-absorption spectrum of B the effect is much weaker in which the screening of the 1*s* core hole is much more efficient due to the higher density of states at the Fermi level in the ground state. The *K*-absorption process is predicted have a tendency to lower the critical temperature T_c of the superconductivity.

DOI: 10.1103/PhysRevB.66.165114 PACS number(s): 71.20.−b, 78.70.−g, 74.70.−b

INTRODUCTION

Surprisingly, magnesium diboride has been shown to possess superconducting properties below the critical temperature $T_c = 39\,\mathrm{K}$.[1] Furthermore, on going from $Mg^{11}B_2$ to $Mg^{10}B_2$ the increase of 1 K in the critical temperature has been observed indicating that the isotope variation of boron is important and the phonon effects are crucial in this case.[2] An interesting point is that the value of T_c is at least two times as large as those of the usual Bardeen-Cooper-Schrieffer (BCS) superconductors. The assumed strong electron-phonon coupling of this compound,[3,4] which is metallic at room temperature, has given rise to a large number of electronic structure calculations.[5–10] The new results have been quite similar to the earlier ones[11,12] giving confidence for the ground state band structure of MgB_2. Also, the angle-resolved photoemission spectroscopy experiments show good agreement with calculations based on the theoretical one-electron approximation[13] suggesting that the possible correlation effects are weak.

Recently, the first single crystals of magnesium diboride have been made.[14] In the future, this provides an opportunity to measure the polarized *K*-emission and absorption spectra giving much more detailed and accurate knowledge concerning the electronic structure of this compound.[15] Due to the anisotropic character of the hexagonal crystal structure,[16,17] one would expect that the spectra should be dependent on the polarization vector **e** of the radiation whether it is parallel ($\mathbf{e}\parallel\mathbf{c}$) or perpendicular ($\mathbf{e}\perp\mathbf{c}$) to the *c* axis reflecting the p_z- or $p_{x,y}$-like states, respectively. In the present study we calculate the corresponding polarized *K*-emission spectra in the ground state and the absorption spectra also in the excited state, when the 1*s* electron has been moved to the empty conduction band.

DETAILS OF CALCULATIONS

The electronic structure calculations were performed using the scalar-relativistic tight-binding linear muffin-tin orbital method in the atomic sphere approximation (ASA).[18] The valence states consisted of Mg 3*s*, 3*p*, and 3*d* states and B 2*s*, 2*p*, and 3*d* states. The supercell contained six atoms. When the effect of the core hole was investigated, the cells containing 3 and 24 atoms were also used. The ratio of the radii of the atomic spheres was $R_B/R_{Mg} = 0.85$. The lattice parameters used were $a = b = 3.086$ Å and $c = 3.524$ Å.[1] For the exchange-correlation potential the Ceperley-Alder form parametrized by Perdew and Zunger[19] was used. The number of *k* points was 1859 in the whole Brillouin zone. Absorption spectra were calculated using both the ground state and the excited state.

The intensity of the x-ray emission (XES) and absorption spectra (XAS) is determined by the density of the electronic states and the matrix element $\langle f|e^{-i\mathbf{k}\cdot\mathbf{r}}\mathbf{e}\cdot\mathbf{p}|i\rangle$, where $\langle f|$ and $|i\rangle$ refer to the final and initial one-electron states, respectively, **k**, **e**, **r**, and **p** are the wave vector and the polarization vector of the photon and the position and momentum operator of the electron, respectively.

According to the Fermi's golden rule, the intensity of the x-ray emission spectrum in the dipole approximation can be written as

$$I(E,\mathbf{e}) \sim E^3 \sum_{f,i} |\langle f|\mathbf{e}\cdot\mathbf{r}|i\rangle|^2 \delta(E_f + E - E_i), \tag{1}$$

where E_i and E_f are the energy eigenvalues of the initial and final one-electron states involved in the radiative transition. The expression (1) can also be used for the calculation of the polarized x-ray absorption spectrum provided the intensity on the left hand side of the formula is replaced by the linear absorption coefficient. XES and XAS are powerful methods to investigate electronic properties of materials. (1) In the dipole approximation the initial and final electronic states are coupled with the selection rule ($\Delta l = \pm 1$). (2) Due to the core state involved in the transition the method is sensitive to the atomic type. (3) The symmetry of the electronic states can be investigated using polarized x rays. For instance, the σ and π bands of B in MgB_2 could be probed separately by this method using $\mathbf{e}\perp\mathbf{c}$ and $\mathbf{e}\parallel\mathbf{c}$, respectively.

The polarized dipole spectra shown in the present paper have been obtained by the x-ray spectrum program (XSPEC) (Refs. 20 and 17) within the so-called final state rule.[21] According to this rule the spectra can be approximated using the final state potential in the single particle calculations. This means that for emission the potential is the same as that of the ground state because there is no core hole in the final

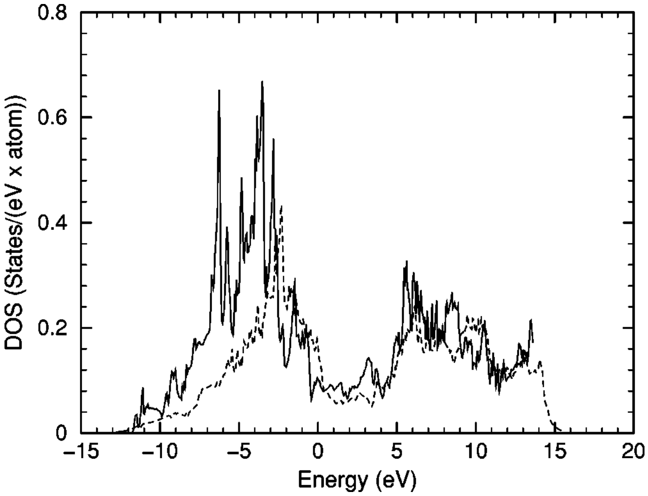

FIG. 1. The local boron *p*-DOS at a B site in MgB_2. The solid line is for the excited state with the B 1*s* core-hole and the dashed line describes the corresponding ground state case without the core hole.

state. For absorption, however, the final state contains a localized core-hole and it may sometimes cause significant relaxations on the conduction band and thus on the whole absorption spectrum.

RESULTS AND DISCUSSION

Let us first consider the changes in the boron *p*-partial density of states (*p*-DOS) due to the core-hole in the B 1*s* state. To elucidate the effects of the core hole concentration on the DOS the calculation was repeated for 3, 6, and 24 atoms per supercell. In the first case, when the excited B atom concentration is 50%, the main peak above the Fermi level is shifted considerably downwards compared to the corresponding ground state peak.

Turning now to the situation when the excited B atom concentration is 6%, one can see from Fig. 1 that by increasing the supercell to consist of 24 atoms the features above the Fermi level have approached to the ground state result, showing no major differences between the core ionized and the ground state cases. This shows that the boron core-hole potential is very efficiently screened. Roughly speaking, one can say that the covalently bound boron atoms on the basal plane share their valence electrons. This means that not only the excited atom but also the neighboring atoms are important. Therefore, in the calculations the number of core-ionized atoms should be such that at least their nearest neighbors are in the ground state.

Contrary to the boron case, in magnesium the screening of the 1*s* core hole potential is a weak and local process in the sense that the interactions between Mg atoms are not significant. The contribution of the electrons of the neighboring atoms to the process is quite small for Mg. Indeed, the weight of the features of the unoccupied part of the *p*-DOS have been considerably shifted to smaller energies as shown in Fig. 2. These results indicate that the effect of the core hole potential is much more important for the *K*-absorption spectra of magnesium than it is to those of boron.

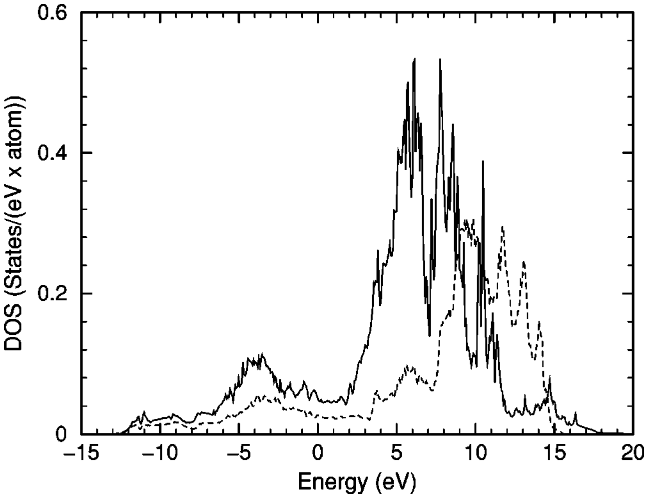

FIG. 2. The local magnesium *p*-DOS at a Mg site in MgB_2. The solid line denotes the situation with the Mg 1*s* core hole and the dashed line is without the core hole.

As Figs. 1 and 2 show the total area under the ground state *p*-DOS curve is smaller than the corresponding total area in the core hole case. This is due to screening effects. At the excited atom site the influence of the core hole is to shift energy bands to lower energies and to increase the weight of the wave functions. Both of these phenomena modify the local *p*-DOS compared to the ground state case.

The polarized x-ray *K* emission spectra of B calculated in the dipole approximation (1) for the ground state of MgB_2 (without the lifetime and phonon broadening of the 1*s* and valence states) can be seen in Fig. 3. The emission spectrum refers to the occupied states below the Fermi energy locating at 0 eV. The $2p_{x,y}$-like states, describing σ type bands, are much more pronounced compared with the $2p_z$ valence bands having π character and the resulting anisotropy can be clearly seen.

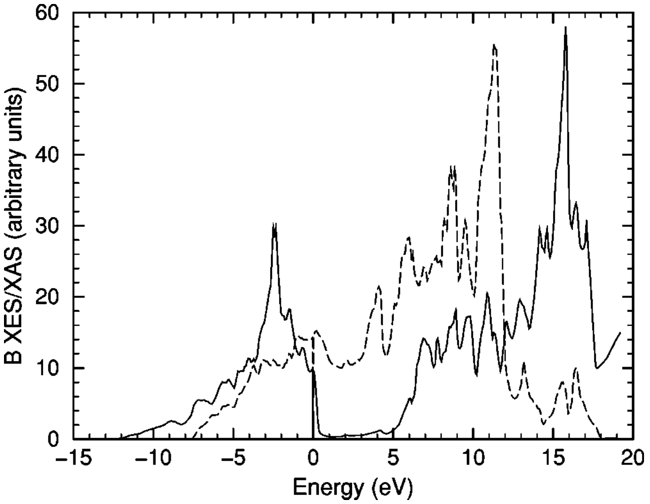

FIG. 3. The polarized *K*-emission and absorption spectra of boron in MgB_2 calculated in the ground state. The solid line is for the *x*, *y* and the dashed line is for the *z* polarization, respectively.

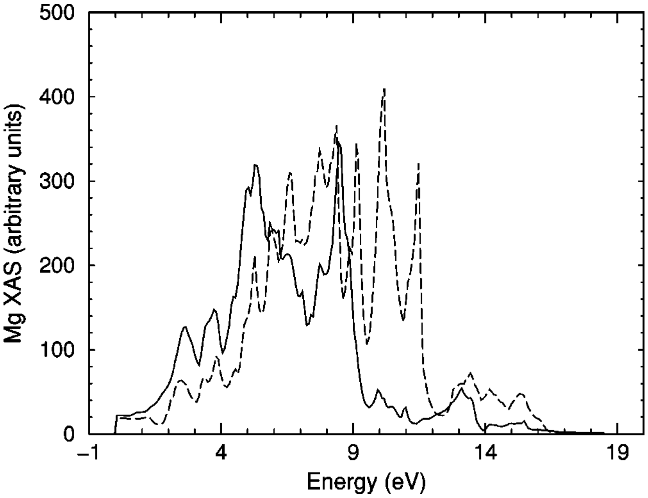

FIG. 4. The polarized *K*-absorption spectra of Mg in MgB_2 calculated with the 1*s* core hole. The solid line describes the *x, y* polarization. The dashed line is for the *z* polarization.

The polarized *K* absorption spectra of boron are also shown in Fig. 3 ($E \geqslant 0$ eV). The dashed line describes the polarization along the *z* axis which means that $\mathbf{e}\perp\mathbf{c}$, and the solid one is for the *x*,*y* plane having $\mathbf{e}\perp\mathbf{c}$. The most striking property for these spectra is that the p_z-like states are dominating close to the Fermi level whereas the $p_{x,y}$ type states are more pronounced away from the *K* absorption edge. These results are in good agreement with the interpretation of the experimental unpolarized *K* absorption spectrum of boron in MgB_2 (Refs. 22 and 23) finding that the unoccupied states up to 4 eV above the Fermi level can be explained by the p_π states. According to Fig. 3, a significant difference between the *x, y*, and *z* polarizations of the line shape at the absorption threshold is expected. Since the Fermi level is located at the steep slope of the ground state *p*-DOS (Fig. 1), the measurement of the polarization of the absorption could give information on the possible many-body effects[24] as well as on the validity of the final state rule.

Since the Mg ion has lost the main part of its valence electrons,[4,25] the intensity of the *K*-emission spectrum is expected to be small. Thus we only focus on the polarized *K* absorption which are shown in Fig. 4. The calculations have been performed for a Mg atom with a 1*s* core hole in the supercell of six atoms, the extra electron being added in the valence band to maintain the charge neutrality of the supercell. The *x*,*y*-polarized absorption dominates just above the edge whereas the *z* component is stronger far away in energy which is the opposite to that for the polarized *K* absorption spectra of boron in Fig. 3. The effect of the core-hole potential is to bring the features of Mg about 4 eV closer to the Fermi level compared with the corresponding ground state case which can be seen from Fig. 2.

It has been shown that doping magnesium diboride with carbon atoms lowers the critical superconducting transition temperature T_c for $MgB_{2-x}C_x$.[26] This is due to the smaller density of states at the Fermi level (for the latter compound).[26] It is well known that the valence configuration of the core level excited atom with the valence *Z* is quite identical with that of the $Z+1$ atom in the ground state as far as the *s*-*p* metals are concerned. If we remove an inner 1*s* electron, then this process is almost indistinguishable from a unit increase in nuclear charge, the extra electron being now on the valence orbital. Now, using these arguments[27] one could replace the doping C atom by the core ionized boron one, since the valence configuration of the carbon atom in the ground state is similar to that of the boron atom in the excited state of the *K* absorption. This is called the $Z+1$ approximation, where the core hole has been replaced by a proton. The results of our calculation in Fig. 1 support this argument in the sense that the *p*-DOS of boron at the Fermi level of the ground state MgB_2 is 0.166, states/eV whereas the corresponding value in the case of the B 1*s* core-hole (using 24 atoms per supercell) is much lower being 0.118 states/eV.

Experimentally, it has been shown that for the $Mg_{1-x}Al_xB_2$ compound the superconducting properties occur at lower temperatures than for MgB_2. This is explained by the smaller density of states at the Fermi level for the former one.[28] Using once again the $Z+1$ approximation, since Al is the next heavier atom to Mg, the *K*-absorption process for magnesium should result in lower T_c for MgB_2 as well. This lowering of T_c, however, can depend on the intensity of the incident x rays and the lifetime of the 1*s* core hole.

In conclusion, for B the empty p_z orbitals are closer to the Fermi level than the $p_{x,y}$ states. In the case of Mg the situation is just the opposite. The screening of the 1*s* core-hole in B is almost complete involving the neighboring boron atoms as well, whereas in Mg it is incomplete and rather insensitive to the state of the neighboring magnesium atoms. Providing these two extreme cases, MgB_2 is an ideal material to analyze the final state rule for the x-ray absorption spectra provided experimental data for Mg would be at disposal, too.

ACKNOWLEDGMENTS

We are grateful to H.L. Skriver for giving his TB-LMTO code. The calculations were made using the computational facilities provided by the Center for Scientific Computing, Espoo, Finland.

---

[1] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) **410**, 63 (2001).
[2] S. L. Bud'ko, G. Lapertot, C. Petrovic, C. E. Cunningham, N. Anderson, and P. C. Canfield, Phys. Rev. Lett. **86**, 1877 (2001).
[3] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, Phys. Rev. Lett. **86**, 4656 (2001).
[4] J. M. An and W. E. Pickett, Phys. Rev. Lett. **86**, 4366 (2001).
[5] P. Ravindran, P. Vajeeston, R. Vidya, A. Kjekshus, and H. Fjellvåg, Phys. Rev. B **64**, 224509 (2001).
[6] P. P. Singh, Phys. Rev. Lett. **87**, 087004 (2001).

[7] N. I. Medvedeva, A. L. Ivanovskii, J. E. Medvedeva, and A. J. Freeman, Phys. Rev. B **64**, 020502 (2001).

[8] M. J. Mehl, D. A. Papaconstantopoulos, and D. J. Singh, Phys. Rev. B **64**, 140509(R) (2001).

[9] K. D. Belashchenko, M. van Schilfgaarde, and V. P. Antropov, Phys. Rev. B **64**, 092503 (2001).

[10] G. Satta, G. Profeta, F. Bernardini, A. Continenza, and S. Massidda, Phys. Rev. B **64**, 104507 (2001).

[11] D. R. Armstrong and P. G. Perkins, J. Chem. Soc., Faraday Trans. 2 **75**, 12 (1979).

[12] A. L. Ivanovskii and N. I. Medvedeva, Russ. J. Inorg. Chem. **45**, 1234 (2000).

[13] H. Uchiyama, K. M. Shen, S. Lee, A. Damascelli, D. H. Lu, D. L. Feng, Z.-X. Shen, and S. Tajima, Phys. Rev. Lett. **88**, 157002 (2002).

[14] S. Lee, H. Mori, T. Masui, Y. Eltsev, A. Yamamoto, and S. Tajima, J. Phys. Soc. Jpn. **70**, 2255 (2001).

[15] G. Dräger, R. Frahm, G. Materlik, and O. Brummer, Phys. Status Solidi B **146**, 287 (1988).

[16] P. Rennert, H. Schelle, and U.-H. Gläser, Phys. Status Solidi B **121**, 673 (1984).

[17] R. Laihia, K. Kokko, W. Hergert, and J. A. Leiro, Phys. Rev. B **58**, 1272 (1998).

[18] O. K. Andersen, O. Jepsen, and D. Glötzel, *Proceedings of the International School of Physics "Enrico Fermi," Course LXXXIX, Highlights of Condensed-Matter Theory*, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, Amsterdam, 1985), p. 59.

[19] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[20] W. Hergert, K. Kokko, and R. Laihia (unpublished).

[21] U. von Barth and G. Grossmann, Phys. Rev. B **25**, 5150 (1982).

[22] J. Nakamura, N. Yamada, K. Kuroki, T. A. Callcott, D. L. Ederer, J. D. Denlinger, and R. C. C. Perera, Phys. Rev. B **64**, 174504 (2001).

[23] T. A. Callcott, L. Lin, G. T. Woods, G. P. Zhang, J. R. Thompson, M. Paranthaman, and D. L. Ederer, Phys. Rev. B **64**, 132504 (2001).

[24] M. H. Heinonen and J. A. Leiro, Philos. Mag. B **46**, 669 (1982).

[25] E. Z. Kurmaev, I. I. Lyakhovskaya, J. Kortus, A. Moewes, N. Miyata, M. Demeter, M. Neumann, M. Yanagihara, M. Watanabe, T. Muranaka, and J. Akimitsu, Phys. Rev. B **65**, 134509 (2002).

[26] V. P. Antropov, K. D. Belashchenko, M. van Schilfgaarde, and S. N. Rashkeev, cond-mat/0107123 (unpublished), and the references therein.

[27] N. D. Lang and A. R. Williams, Phys. Rev. B **16**, 2408 (1977).

[28] J. S. Slusky, N. Rogado, K. A. Regan, M. A. Hayward, P. Khalifah, T. He, K. Inumaru, S. M. Loureiro, M. K. Haas, H. W. Zandbergen, and R. J. Cava, Nature (London) **410**, 343 (2001).