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Core-hole effects on the B K edge in MgB_2

B Jiang, N Jiang and J C H Spence

Department of Physics and Astronomy, Arizona State University, Tempe, AZ, 85287-1504, USA

E-mail: jiangb@asu.edu

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Abstract

The projected density of states (DOS) for the ground and excited states of boron in MgB_2 has been calculated using the augmented plane wave plus local orbital method. The core-hole interaction is found to have a significant effect on the B $p_x p_y$ states, but has little effect on the more metallic B p_z states. The unoccupied B $p_x p_y$ DOS near the Fermi level decreases as a function of core-hole strength. Comparisons with experimental electron energy loss spectra of the B K edge show that a simulation with half a core hole provides the best approximation to the final states in MgB_2.

1. Introduction

The discovery of type II superconductivity in MgB_2 ($T_c \sim 39$ K) [1] has attracted considerable interest because of its high upper critical field at temperatures (around 20 K) which can be attained using a closed-cycle refrigerator, and its usefully low normal-state resistivity, allowing better tolerance to quenching. Much work has concentrated on the superconductivity mechanism in this binary metallic compound. Boron isotope experiments suggests a BCS-type superconductor [2]. In BCS theory, T_c is reduced for lighter elements, smaller Debye frequencies, stronger electron–phonon coupling and a large density of states (DOS) at the Fermi level. Evidence from x-ray photoemission spectroscopy indicates multiple superconducting gaps in MgB_2 and a deviation from the conventional isotropic s-wave mechanism [3]. Band structure calculations reveal two distinct valence bands in the two-dimensional covalent in-plane σ-subband (B $2p_x p_y$) and a three-dimensional metallic-type interlayer π-subband (B $2p_z$) [4, 5]. The σ-subband has the highest DOS near the Fermi level, extending 0.8 eV above, which is predominantly of $p_x p_y$ character. These $p_x p_y$ states are thought to play a major role in the superconductivity of MgB_2 [6], and experimental confirmation of the existence of empty $p_x p_y$ states near the Fermi level has become important. Recently, experimental evidence obtained using x-ray absorption spectroscopy (XAS) and electron energy loss spectroscopy (EELS) has been reported. However, core-hole effects were ignored in these measurements [7, 8].

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In XAS and EELS, a core electron is excited from an atomic-like core orbital into previously unoccupied bands above the Fermi level. Due to the atomic-like initial core orbital, spectra obtained by both XAS and EELS are normally considered to be proportional to the site- and symmetry-projected DOS of final states if dipole selection rules are satisfied. However, the core-hole interaction complicates the density of final states and may result in misinterpretation if the ground state DOS is used. An understanding of core-hole effects in each specific material is essential for the interpretation of spectra from XAS and EELS.

In this paper, we discuss core-hole effects on EELS of the B K edge in MgB_2. The experimental EELS is compared qualitatively with theoretical simulations based on several core-hole approximations. Core-hole effects on the density of final states are also examined, on the basis of band structure calculations.

2. Theoretical calculations

Band structure calculations were performed using the method of augmented plane waves plus local orbitals (APW + lo) [9], encoded in the Wien2K software [10]. The major advantage of APW + lo is that it converges faster and reaches the same accuracy as the linearized augmented plane wave (LAPW) method while using the same number of plane waves [11]. Exchange and correlation effects are treated within density functional theory, using the generalized gradient approximation (GGA) [12]. Muffin tin radii of 2.0 au for Mg and 1.65 au for B were used. The Brillouin-zone integration was performed using a modified tetrahedron method [13].

EELS simulations were carried out by calculating the differential cross-section using the Fermi golden role. For small-angle scattering, the dipole approximation applies. Therefore, the EELS intensity can be written as the product of a DOS and an atomic transition matrix:

$$I(E, \vec{q}) \propto |\langle f|\vec{q}\cdot\vec{r}|i\rangle|^2\rho(E) \propto \vec{q}\cdot|\langle f|\vec{r}|i\rangle|^2\rho(E)$$

where $|i\rangle$ and $|f\rangle$ represent the initial and final states of the excited electron, $\rho(E)$ is the unoccupied DOS and $\vec{q}$ is the momentum transfer. In order to simulate core-hole effects, a $2 \times 2 \times 2$ supercell (containing 16 B and 8 Mg atoms) was constructed and the excited B atom in the supercell was treated as an impurity. Two approaches have been used to describe the excited final states: the $Z + 1$ and the final state approximation. In the $Z + 1$ approximation, the core hole is simulated as an extra nuclear charge at the excited atom site [14]. In the final state approximation, a single or partial core electron at an excited atom site (e.g. one 1s orbital in a B atom) is removed from the core orbital to the valence band. The ion core is free to relax in self-consistent field (SCF) calculations [10]. This method can also be used to simulate, for example, the effect of half a core hole [15]. It is most useful for metal crystals where free electron screening effects are strong [15, 16].

3. Experiment

Samples of MgB_2 were sintered from magnesium and boron powders under a pressure of 3.0–5.0 GPa and at a temperature of 900–1000 °C. (Details are given elsewhere [17].) TEM specimens were prepared by tripod polishing, followed by brief (5 min), low-energy (2.5 kV) ion milling (for cleaning surfaces). No radiation damage due to ion milling was observed. The spectra from EELS of the B K edge were recorded using a VG 501 scanning transmission electron microscope (STEM) operating at 100 keV with a cold field emission gun (FEG) and a Gatan digital parallel electron energy loss spectrometer (PEELS). The energy resolution was about 0.6 eV (FWHM of zero-loss peak). The collection semi-angle is about 2.5 mrad and the convergence semi-angle is about 10 mrad. The average grain size was about 0.1 μm.

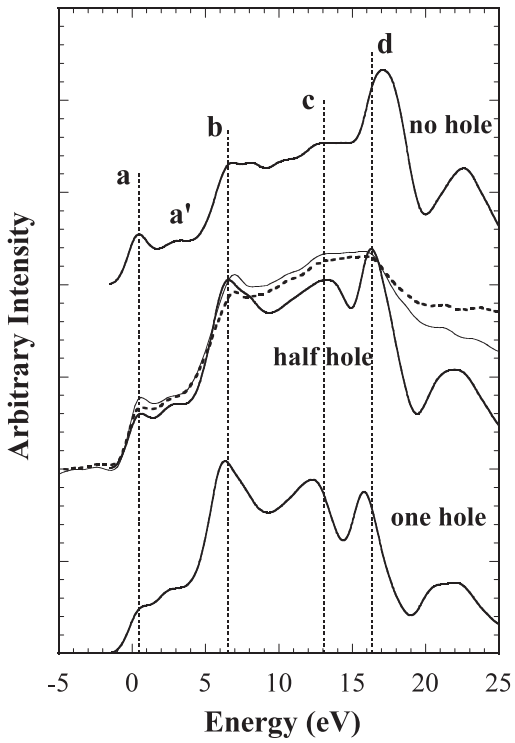

Figure 1. Comparison of experimental spectra from EELS (dashed curve for as-recorded spectrum and thin solid curve for deconvoluted spectrum) with electronic structure calculations (thick solid curves) for three cases: core hole, half a core hole and one core hole. Note the intensity and position changes of features a, b, c and d with core-hole strength.

The acquisition area of 0.3 by 0.3 μm, which was defined by scanning a raster, contains several randomly oriented MgB_2 grains, which was also confirmed by electron diffraction. Power-law backgrounds were fitted and subtracted from all spectra [18]. To reduce the noise due to channel-to-channel gain variation of the photodiode detector array, a series of spectra were acquired, with each spectrum shifted prior to acquisition by 1 eV relative to the previous spectrum. (1 eV is not equal to the interdiode spacing). The resulting spectra were realigned before being added together.

4. Results and discussion

The spectra from EELS of the B K edge in MgB_2 were simulated using the final state approximation for several conditions: ground state (ignoring core-hole effects), half a core hole and single core hole. The results are plotted in figure 1. The simulated spectra were broadened to 0.6 eV to match the energy resolution in the experiments. The experimental EELS of the B K edge is also shown in figure 1 (dashed curve), along with the spectrum (thin solid curve) after deconvolution of plural scattering using the Fourier-ratio method [18]. In the low-energy regime (<20 eV), several features were observed in both the measured and calculated spectra, indicated by letters. The core-hole interaction strongly affects the relative intensities of peak a, peak b and peak d. Peak a is weaker in the calculation using half a core hole than in that based on the ground state, and disappears when a single core hole is used. The

relative intensity of peak b and peak d alters as a function of core-hole strength: with increasing core-hole strength, the intensity of peak b increases but that of peak d decreases. Additionally, the core-hole interaction also affects the peak positions: most peaks shift towards the Fermi energy with increasing core-hole strength. We note that the position and intensity of peak a′ seems to be independent of the core-hole strength. Considering all the peak positions and their relative intensities, the inclusion of half a core hole is seen to result in substantial improvement over both the ground state and single-core-hole calculations [19]. This result differs from that of Zhu *et al* [8], who concluded that core-hole effects are not present for the B K edge in MgB_2. Core-hole effects were also examined under the $Z+1$ approximation, and the calculated spectrum of the B K edge was found to be very similar to that of a single-core-hole simulation, in which the core-hole effects are overestimated. (The results are not shown.)

In the high-energy regime (>20 eV), however, a discrepancy between the measured and calculated spectra is noted. This is probably due to the plural scattering induced by the energy loss of plasmon excitations in experiments, which is peaked around 20 eV. The removal of plural scattering did improve the fitness. In addition, the final state lifetime effects may also cause further broadening [20]. However, we do not include final state broadening in this study.

Figure 2 shows calculations of the core-hole effect on the DOS projected on the B p_xp_y and p_z states in MgB_2 under the ground state, half-core-hole and single-core-hole approximations. The calculated ground state DOS is in agreement with other calculations [4]. The most important feature of the B p_xp_y states is the large DOS near the Fermi level, extending about 0.8 eV above it, with a FWHM width of about 0.5 eV. Then a deep minimum (pseudogap) about 4–5 eV wide appears, separating the p_xp_y states into valence and conduction bands. These features are common to diboride compounds, which are considered to represent the strong chemical interaction of B–B covalent σ-bonding [21]. In contrast, B p_z states are metallic, with fewer features above the Fermi level. An interesting finding is that the p_z DOS shows strong intensity in the 'pseudogap' region of the p_xp_y states. In other words, the contribution to the p DOS within this energy region is mainly from p_z states. It produces a small peak 3 eV above the Fermi level (marked as a′).

In principle, the EELS and XAS of the core edge probe the density of unoccupied states. However, the core-hole interaction can strongly modify the DOS of the final states in insulators [22] and semiconductors [23]. Furthermore, it has been shown that the core hole in Cu metal is partially screened by the valence electrons [15, 24]. In figure 2, the modification of the p DOS of the B site due to half a core hole and a single core hole are compared with the ground state DOS.

It is seen that the core-hole interaction strongly affects only the B p_xp_y and Mg DOS (not shown here), but has little effect on the B p_z DOS. The intensities and positions of the peaks marked a, b, c and d change significantly as a function of core-hole strength. For example, the FWHM of the empty p_xp_y states near the Fermi level (marked as a) decreases from 0.5 eV in the ground state calculation to 0.25 eV in the final state calculation with half a core hole, and eventually disappears in the final state calculation with a single core hole. In addition, the intensity of this DOS also drops with increasing core-hole strength. In contrast, no significant change is observed for the p_z DOS above the Fermi level with the core-hole strength. This is probably because the p_z states are metallic in character.

The above findings demonstrate the power of techniques such as EELS and XAS in combination with electronic structure calculations for the study of ground state electronic structures. In this study, we show that the final states are best approximated by half a core hole in MgB_2. In this case, the integrated intensity of the B p_xp_y states in the 'pseudogap' region (0–4 eV) is only about one fifth of that of the p_z states. Using the half-core-hole calculation, the population in the occupied p_z and p_xp_y subbands increases by 0.13

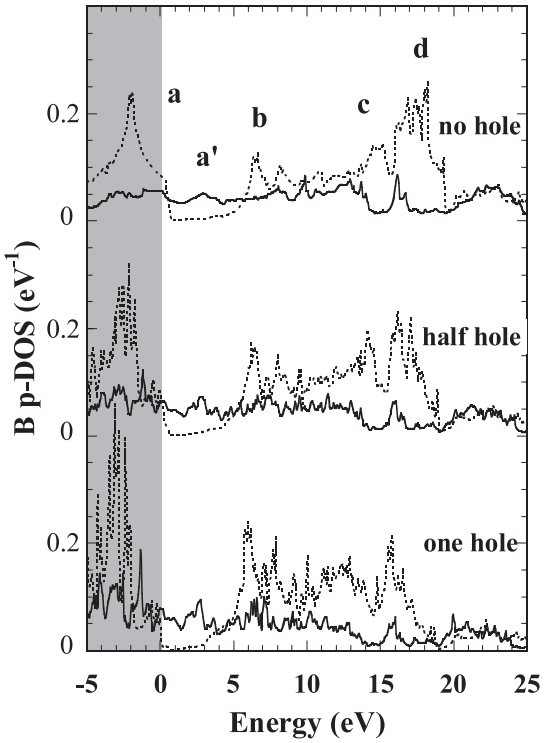

Figure 2. Core-hole effects on the symmetry-projected DOS of $p_x p_y$ (dotted curves) and p_z (solid curves) obtained from band theory calculations. The main features are marked by letters corresponding to those in figure 1. Note the intensity and position changes of peaks a, b, c and d with the core-hole strength.

and 0.2 electrons respectively, for a total of a 0.33 electron increase in the occupied B p subband. To confirm this interpretation, we therefore plan observations of the unoccupied B $p_x p_y$ states close to the Fermi level using orientation-dependent EELS or XAS measurements with both high energy resolution (<0.2 eV) and high spatial resolution ($<0.1\mu$m).

5. Conclusions

The EELS of the B K edge of MgB_2 has been simulated using the APW + lo method while varying the strength of a B core-hole contribution. Comparisons with experimental measurements show that the best fit is obtained using half a core hole. These core holes have a significant influence on the symmetry-projected B $p_x p_y$ DOS, but little effect on the more metallic B p_z DOS, a finding which may be important for our understanding of superconductivity in this material.

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