Characteristics of X-ray Absorption Near-edge Spectra Obtained from Various MgB₂ films

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X-ray absorption near-edge spectrum (XANES) of various MgB₂ films prepared under different procedures has been measured by using synchrotron radiation. By comparing to the band structure calculation we observed that the major spectral peaks of B K edge XANES resulted from the empty states with p characters of boron in MgB₂. The spectral peak near the threshold indicates the existence of the hole states in the valence band at the Fermi level. This is particularly clear in some c-axis oriented films. The peaks of B_2O_3 were common peaks in all of the films we studied, indicating the contamination of B_2O_3 . This peak sometimes will smear the main spectral structure of MgB_2 if it is seriously contaminated. The experimental XANES of Mg K edge results from the empty states with Mg p characters can be identified by comparing the experimental spectrum with the band structure calculations. A small core-hole effect resulted from the less electron screening of the Mg ions in MgB_2 can be identified. There are empty states, as appear in the threshold spectral structure, extended from the Fermi level indicates the metal characters of Mg in MgB₂. Little anisotropic characteristics between $p_{x,y}$ and p_z can be identified from the polarization-dependent measurements, except the spectral intensity around 1314 eV. Around that energy, the spectral intensity is higher for the electric field of the beam parallel than perpendicular to the boron planes, in accordance with the band structure calculations.

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I. INTRODUCTION

Since the discovery of the superconductivity of MgB₂ [1], many works have been done in order to understand the precise mechanism of its record-high value of the superconducting temperature (40 K) among the binary intermetallic compounds.

It is known that MgB₂ is a metal with a layer structure with alternating layers of boron and magnesium atoms. The boron atoms form honeycombed layers similar to the layers of graphite, with sp² hybridization bonds (σ - bonds) and the p_z bonds (π - bonds).

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© 2007 THE PHYSICAL SOCIETY OF THE REPUBLIC OF CHINA The magnesium atoms are located above the center of the hexagons in-between the boron planes. The magnesium atoms will transfer charges to boron atoms and the boron will have enough electrons to form the σ - bonds and π - bonds. In fact the electronic structure calculated on the basis of a fictional system ²⁺B₂ is very similar to that of MgB₂[2], except that σ - bonds are completely filled as the σ - bonds in graphite. It is known that the graphite can become superconducting up to 5 K when doped (intercalated) [3]. Several different ab initio band calculations show that the σ -bonds and π -bonds of MgB₂ are not completely filled at the Fermi level [2, 4-7]. The energy position of the B σ (2p_{x,y}) bands at the point of Brillouin Zone lie above the Fermi level and form hole-type cylindrical elements of the Fermi surface [8]. The B 2p_z states are perpendicular to the boron plane and responsible for the weak interlayer π bonds. Both σ and π bands of B are suggested to be critical for the description of the mechanism of the superconductivity of MgB₂[8, 9].

One also notices that magnesium states in MgB₂ are important to understand the charge transfer mechanism of Mg to B. A hybridization of B $2p_z$ level and Mg 2p level will lower the former while raising the latter. This hybridization effect lowers the $\pi(p_z)$ bands relative to the bonding σ bands and cause $\sigma \rightarrow \pi$ charge transfer, resulting hole doping in σ band and deriving the superconductivity in MgB₂ [2].

The unoccupied states with p character close to the Fermi level can be easily probed by the K X-ray absorption near-edge spectrum (XANES) because of the dipole transition rule. By using the technique of X-ray absorption spectroscopy on films of MgB₂ one can look into the partial density of states (PDS) above the Fermi level. If the film has c-axial oriented crystalline structure one can use polarized X-ray to probe the PDS parallel to the boron/magnesium planes (ab plane) and perpendicular to the planes. In other words, one can probe the empty states of $p_{x,y}$ and p_z .

Nevertheless, fabricating films of MgB₂ is not an easy task since MgB₂ is not easily stabilized substances. Contaminations will attribute to the characteristics of the XANES of MgB₂ films. We report our study of various films of MgB₂ fabricated by different method by XANES and show that the main characteristics of the XANES will be disturbed little, if any, by the contaminations. The characteristics of XANES will indicate the characteristics of the PDS (the electronic structure) of MgB₂.

II. EXPERIMENTS

II-1. Samples

In this work, MgB₂ films were made by different methods: Samples S1 and S2 were obtained by post-annealing a precursor film in either an oxygen-free copper cell (for S1) or an ultra-high vacuum comparable stainless steel cell (for S2) under magnesium vapor at about 700°C (S1) and 800°C (S2) [12]. The precursor film was made by ion sputtering a Mg-rich MgB2 target on a substrate of R-plane Al_2O_3 single crystal. The sample S3 was obtained by post-annealing a precursor film in a tantalum tube under a saturated magnesium vapor at about 900°C [10]. The precursor film was made by laser ablation of boron on a substrate of R-plane Al_2O_3 single crystal. The sample S4 was obtained by the



FIG. 1: The temperature dependent resistances of the samples: the right scales are for S1, S2, and S3, and the left scales are for S4.

hybrid physical-chemical vapor deposition (HPCVD) technique, and a substrate of (0001) 4H-SiC was used [11].

The temperature dependent resistance of these samples is shown in Fig. 1. The superconducting transition temperatures of S1 and S2 are about 25 K with transition width about 2.5 K while the transition temperature of S3 is 39 K with transition width of 0.5 K. S4 has the highest transition temperature of 41.10 K among the investigated samples. Its transition width is 0.16 K. S1 is a film formed by a group of nanoparticles [12], S2 is a polycrystalline film, while S3 and S4 a re c-axis oriented crystalline films.

II-2. X-ray absorption near edge spectra (XANES)

Our soft X-ray absorption spectra were measured at room temperature at the beam line 20A at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The beam line is a spherical-grating-monochromator beam line [13]. Gratings with 400 l/mm and 1200 l/mm were used respectively for the measurements of the K edge absorption of B and Mg. The slits of the beamline monochromator were set to be 30 μ m providing a resolving power of about 1900 by using the 400 l/mm grating and 2100 by using the 1200 l/mm grating.

The experimental geometry is indicated in Fig. 2, where the normal n of the ab plane of the film is indicated. The photon detector is a multichannel plate (MCP) that is sited at 45° with respect to the incident beam (ν_{in}) to detect the outgoing X-ray fluorescence (ν_{out}). In other words, we use a bulk sensitive total-fluorescence-yield (TFY) method to obtain the soft X-ray absorption near-edge spectra (XANES). Simultaneously, the sample current signal is collected. This signal measures the photoelectrons coming out of the sample by the impact of photons. It is a total-electron yield (TEY) method to obtain the XANES. The spectrum obtained by the TEY is surface sensitive due to the short mean free path of





FIG. 2: Top view of the experimental geometry. A linear polarized photon beam with frequency ν_{in} is incident on the sample and the frequency of the outgoing X-ray fluorescence is ν_{out} . n is the surface normal(c-axis). E is the polarization of the incident beam.

the outgoing electrons. The intensity of the incident photons was measured by the current generated by a fresh nickel mesh located in front of the target chamber. By rotating the sample holder we can scan the polarization vector parallel to the ab plane toward the c-axis by varying the angle α from 0° to 75° Note that the normal n will pass the line of ν_{out} for $\alpha > 45^{\circ}$ and the angles α and β are on the same side of normal n.

The energy of the XANES of boron K edge was calibrated by referring to the energy of the resonance peak of B_2O_3 as 193.8 eV, while that of Mg K edge was calibrated by referring to the energy at the inflection point of the K edge of Mg metal as 1303.0 eV. Each spectrum was normalized with the intensity of the incident photons.

The target self-absorption was not corrected. It is proper for the XANES of Mg K edge since the mean free path of the photons in the terget is about 1.2 μ m, much greater than the target thickness (varied from 400 nm to 700 nm) and therefore, the target self-absorption effect can be neglected. The XANES of B K edge may be distorted due to target self-absorption effect since the mean free path of the photons in the target is about 100 nm, smaller than the target thickness. The resonance peak may be suppressed due to a larger self-absorption effect. Besides, the self-absorption effect is also angular dependent [14], which will affect the overall spectral features. Nevertheless, the resonance spectral positions will not be altered. It is difficult to do the self-absorption correction for samples containing impurities. However, the uncorrected spectrum will not affect the conclusions of this work as will be shown later.



FIG. 3: The XANES of B K edge of the samples from (a) TFY measurement and (b) TEY measurement

III. RESULTS AND DISCUSSIONS

III-1. General features of the XANES

The XANES of B K edge for all samples is shown in Fig. 3. They were taken at $\alpha = 45^{\circ}$. The spectrum of B₂O₃ is included for comparisons. Both TFY (Fig.3 (a)) and TEY spectra (Fig.3 (b)) are shown. The peaks resulting from B₂O₃ (the peak D at 193.8 eV) is seen in all samples, it is relatively clear in the TEY spectra. The peak C (191.9 eV) is relatively pronounced in S1. The origin of this peak is not so clear; it had been suggested to be from the inelastic resonance scattering [15] or some kind of surface contaminations [16]. This peak seems to smear out the other peaks, such as peaks A (186.7 eV), B (189.4 eV), and E (210 eV), which are thought to be the peaks resulting from MgB₂. They clearly appear in the other samples. A broad spectral peak between about 195 eV to 205 eV is clearly observable in both spectra of S3 and S4.

The XANES of Mg K edge for all samples is shown in Fig. 4. They were taken at $\alpha = 45^{\circ}$. The spectrum of MgO is included for comparisons. Both TFY (Fig.4 (a)) and TEY spectra (Fig.4 (b)) are shown. MgO contains three peaks located at b (1310.8 eV), d (1318 eV) and f (1329.4 eV). The peak a (1304.3 eV), c (1314.3 eV), and e (1325.4 eV) will be the peaks resulting from MgB₂ if the major impurities of the sample is MgO and B₂O₃. One notices that S1 and S2 contain great amount of MgO, while S3 and S4 contain little.



FIG. 4: The XANES of Mg K edge of the samples from (a) TFY measurement and (b) TEY measurement

III-2. The polarization dependent XANES of S3 and S4

The polarization dependent XANES of S3 and S4 are shown in Fig.5 and Fig.6 respectively for B K edge and Mg K edge. These spectra are further normalized such that the relative spectral height of the high energy portion to the spectral height below the threshold is the same.

In the XANES of B k edge (Fig. 5), the change of the threshold peak A from $\alpha = 0^{\circ}$ to $\alpha = 75^{\circ}$ is mild, while the increase of the spectral intensity of the peak B is apparent. The broad peak between about 195 eV and 205 eV decreases from $\alpha = 0^{\circ}$ to $\alpha = 75^{\circ}$. These variations reveal the anisotropic nature of the electronic structure since the polarization vector of the probe beam is parallel to the ab plane of MgB₂ films at $\alpha = 0^{\circ}$ and varies toward parallel to the c-axis by increasing the angle α to 75°. Therefore, one probes the boron $p_{x,y}(\sigma)$ at $\alpha = 0^{\circ}$ and the $p_z(\pi)$ states at $\alpha = 90^{\circ}$. The experimental arrangement at $\alpha = 90^{\circ}$ is not possible due to the finite size of the detector and the block of the outgoing X-ray florescence by the target itself. The measurement at $\alpha = 75^{\circ}$ is considered to have most information that results from the boron $p_z(\pi)$ states.

The peak A is the sole peak for $\alpha = 0^{\circ}$ up to about 4 eV from the threshold. Its width is about 0.6 eV. The peak position is at 186.7 eV. The appearance of this peak as well as other features of our spectra at different scan angles is in agreement with that reported by Zhang et al. [17], but in disagreement with the data shown by Cepek et al. [18], in which the peak A was not observed. The peak B increases for the increase of the scan angle α . Since essentially there is no peak B observable at $\alpha = 0^{\circ}$, this is especially true for the sample of S4, we suggest that the peak B results entirely from the planes parallel to the c axis of the sample, corresponding to the boron p_z bonds (π bonds). A small structure at B peak location at $\alpha = 0^{\circ}$ for the sample of S3 may result from the misalignment of the c



FIG. 5: The polarization dependent XANES of B K edge of the c-axis orientation samples S3 and S4 at $\alpha = 0^{\circ}$, 45°, and 75°. The spectra have been normalized such that the relative spectral height at high energy portion (around 217 eV) to that below the threshold is the same.

axis of some grains in that sample.

In the XANES of Mg K edge (Fig. 6), the anisotropic feature is much less apparent than what appears in the XANES of B Kedge. The existence of empty states starting 1304 eV is apparent. It indicates the metal-like nature of the Mg ions in MgB₂.

III-3. Comparisons of the XANES and Band structure calculations

The partial density of states (PDS) for boron $p_{x,y}(\sigma)$ and $p_z(\pi)$ states obtained by various band calculations, either based on the full potential augmented plane wave method (FLAPW) [16,19,20] or based on the other methods [21,22] are similar and always shows



FIG. 6: Same as Fig.5 except for the XANES of Mg K edge.

that there are two degenerated states in the boron σ band crossover the Fermi level (without core hole and will be referred to as the ground-state PDS). We compare our spectra with the ground-state PDS calculated by the augmented plane waves plus local orbitals (APW+lo) method, encoded in the WIEN 2K software [23], up to the energy 30 eV above the Fermi level in Fig. 7 and Fig. 8. Lattice parameters of a = 3.089 Å and c = 3.522 Å, and muffin-tin radii of 2.91 au for Mg and 1.68 au for B were used in the calculation. For clarity only the spectra of 0° (Fig.7) and 75° (Fig. 8) of S4 are shown for comparisons. The corresponding binding energies measured from the Fermi level are given in the lower scale for both figures. The Fermi level measured from 1s core level of both the XANES of B K edge and Mg K edge is taken to be the inflection point of the threshold peak (peak A for boron and peak a for magnesium). This assignment is in accordance with the X-ray absorption and X-ray



FIG. 7: The combination drawing of the XANES of both B K edge and Mg K edge at $\alpha = 0^{\circ}$ and the PDS with $p_{x,y}$ characters in the band structure calculations by using WIEN 2K code.

emission study [24] for B K edge in MgB₂.

As shown in Fig. 7, we compare the XANES of both B K edge and Mg K edge at $\alpha = 0^{\circ}$ with the PDS that have $p_{x,y}$ characters obtained by the band structure calculations. The agreements between experiment and theory are very well, although a small energy shift is visible for the XANES of Mg K edge. This spectral shift toward the low energy can be caused by the core-hole effect [25] since Mg in MgB₂ is a partially ionic atom, the interaction of the core-hole potential in the X-ray absorption process can be effective due to less electron screening of the Mg ions.

The peak A thus indicates the narrow hole states in the B $\sigma(2p_{x,y})$ bands lie just



FIG. 8: Same as Fig. 7 except for $\alpha = 75^{\circ}$

above the Fermi level in the valence band. This interpretation is in accordance with recent reports that showed the threshold peak intensity (peak A in our case) in the boron K- edge X-ray absorption spectra of $Mg_{1-x}Al_xB_2$ decreased with the increase of Al doping up to about x = 0.3, consistent with hole filling of the σ band crossover the Fermi level [26, 27]. The hole filling caused the detriment of the superconductivity. Our assignment is also in agreement with the recent report by Klie et al. in using EELS [28], in which the peak A was also demonstrated to have $p_{x,y}$ character.

The metal-like PDS with $p_{x,y}$ characters is revealed by the XANES of Mg K edge. The empty band with $p_{x,y}$ characters around the binding energy of about 13 eV is indicated by the broad peaks in the XANES of B K edge (around 198.5 eV) and Mg K edge (around 1314 eV). Both the peak E and the peak d indicate the band around the binding energy of 22.5 eV. It is clearly shown in this combination drawing that these bands are mixing bands of boron states and magnesium states in MgB₂.

AS shown in Fig. 8, we compare the XANES of both B K edge and Mg K edge at $\alpha = 75^{\circ}$ with the PDS that have p_z characters obtained by the band structure calculations. The agreements between experiment and theory are good even though the spectra contain some contribution from the states with $p_{x,y}$ characters at $\alpha = 75^{\circ}$ (rather than $\alpha = 90^{\circ}$). One specially notes that the peak B reveals the PDS with p_z characters in the band calculations around the binding energy of 3.0 eV. The threshold peak indicates there are hole states near the Fermi level. The appearance of this spectral peak to be shaper than the prediction of the band structure calculation could be due to the contribution from the $p_{x,y}$ states. The spectral energy shift is also shown in the XANES of Mg K edge which again is due to the core-hole effect caused by the less electron screening of the Mg ions.

IV. CONCLUSIONS

In this work we show that the X-ray absorption near-edge spectrum (XANES) of MgB₂ provides information of the electron structure of the empty states above the Fermi level, although the sample may have some impurities, namely B₂O₃ and MgO. The threshold peak of the XANES of B K edge (peak A in Fig.2 and Fig.6) indicates the narrow hole states in the B $\sigma(2p_{x,y})$ bands lie just above the Fermi level. The second peak of the XANES of B K edge (peak B in Fig.2 and Fig.7) indicates empty states with p_z characters about 3.0 eV about Fermi level. The experimental XANES of Mg K edge results from the empty states with Mg p characters can be identified by comparing the experimental spectrum with the PDS of band structure calculations. A small core-hole effect resulted from the less electron screening of the Mg ions in MgB₂ can be identified. There are empty states, as appear in the threshold spectral structure, extended from the Fermi level indicates the metal characters of Mg in MgB₂. Little anisotropic characteristics between P_{x,y} and p_z can be identified from the polarization-dependent measurements of the XANES of Mg K edge.

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