Available online at www.sciencedirect.com
ScienceDirect
Ultramicroscopy 108 (2008) 320–326
ultramicroscopy
www.elsevier.com/locate/ultramic

Investigation of hole states near the Fermi level in $Nb_{1-x}Mg_xB_2$ by electron energy-loss spectroscopy and first-principles calculations

C. Ma, R.J. Xiao, H.X. Geng, H.X. Yang, H.F. Tian, G.C. Che, J.Q. Li*

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

Received 9 January 2007; received in revised form 4 April 2007; accepted 1 May 2007

Abstract

The fine structures of the electron energy-loss spectra (EELS) for the B-K edge have been examined in NbB_2 and superconducting $Nb_{0.75}Mg_{0.25}B_2$. The experimental results are analyzed based on the calculations of density functional theory (DFT) using the Wien2k code. The results of the EELS spectra and the angular decomposition of the density of states (DOS) reveal that both the B p_z and B p_x+p_y states in NbB_2 have large weights at the Fermi energy due to intersheet covalent bonding with notable hybridization between the Nb 4d and B 2p states. This kind of hybridization also results in different core-hole behaviors for the B-K edge in two orthogonal crystallographic orientations. The best fit between experimental and theoretical data is achieved with consideration of the core-hole effect of the B 1 s states, in particular for the $q\perp c$ spectra. Analysis of the electronic structure of the $Nb_{1-x}Mg_xB_2$ superconductors suggests that confinement of the intersheet covalent bonding is likely to be favorable for the improvement of superconductivity in this kind of materials.

PACS: 74.25.Jb; 71.20.−b; 74.62.Dh; 79.20.Uv

Keywords: Electron energy-loss spectra; Density functional theory; $Nb_{1-x}Mg_xB_2$; Superconductivity

1. Introduction

The metal diborides, MB_2 (M = Mg, Nb, Ta, V), have a rich variety of important physical and structural properties as extensively investigated in the past decades [1]. In particular, the discovery of superconductivity in MgB_2 with T_c~39 K [2] gave a considerable impetus to investigate the fundamental properties of the MB_2 family of compounds. It has been demonstrated that the superconductivity in MgB_2 is essentially driven by in-plane hole carriers in B $p-\sigma$ (sp^2) states [3] and the observation of a significant isotope effect favors phonon-mediated superconductivity [4]. Previously, much work was focused on exploitation of new superconductors made from this kind of materials, especially in the transition metal diborides, such as ZrB_2, VB_2, TaB_2, and TiB_2 [5,6]. More recently, superconductivity was observed in $Nb_{1-x}Mg_xB_2$ [7] and $Nb_{1-x}B_2$ materials. For example, $Nb_{1-x}B_2$ with $x=0.24$ has a critical transition temperature of T_c~9.2 K due to the emergence of B $p-\sigma$ hole states [8], which is similar to the superconductor MgB_2 where the superconductivity disappears when the B $p-\sigma$ hole states are completely filled by electrons through Al doping [9,10]. However, for $Nb_{1-x}Mg_xB_2$ [7], the situation differs in that superconductivity occurs with the charge carriers being not holes but electrons. In order to clearly understand the superconductivity of MB_2 materials with either hole or electron carriers, many theoretical and experimental investigations have been done to study the characteristics of the electronic states near the Fermi level (E_F) in these materials [5,11].

Electron energy-loss spectroscopy (EELS) [12] is a well-established technique for retrieving fundamental information about the chemical bonding, electronic structure, and charge distribution at scales as small as a few nanometers. The orientation-dependent electron energy-loss near-edge structure (ELNES) in particular can give clear information about the anisotropy of the hole states near E_F [13]. In

*Corresponding author. Tel.: +86 10 82649524; fax: +86 10 62561422.
E-mail address: Ljq@aphy.iphy.ac.cn (J.Q. Li).

0304-3991/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultramic.2007.05.003

previous publications, the in-plane p−σ states in MgB_2 have been extensively examined using orientation-dependent EELS [9,14,15]. However, the contribution of the out-of-plane p−π (p_z) states to superconductivity is still ambiguous in these layered materials [16]. In the present work, the anisotropic features of the electronic states around E_F for NbB_2 have been examined by orientation-dependent B-K edge EELS and analyzed based on electronic structure calculations. The influence of Mg doping on the electronic structure of $Nb_{1-x}Mg_xB_2$ will be discussed in connection with the material's superconducting properties.

2. Computational details and experimental methods

The calculations of the electronic structure and the electron ELNES were carried out by using the full potential linear augmented plane wave (LAPW) method within density functional theory (DFT) in which the exchange and correlation effects were treated by using the generalized gradient approximation (GGA) via the Wien2k code [17] equipped with the TELNES.2 program [18]. The structural parameters of NbB_2 crystal were cited from Ref. [7] for our calculations. The muffin-tin radii R_{mt} were selected as 1.6 a.u. for B atoms and as 2.2 a.u. for Nb atoms. The maximum angular momentum of the radial wave functions (l_{max}) was chosen as 10 and $R_{mt}K_{max}$ was fixed at 8.0 to determine the basis size. We used 1020 irreducible Brillouin-zone k points for the primitive cell and 126 irreducible k points for the $2\times2\times2$ supercell when calculating the spectra.

In the experimental EELS measurements, we used an FEI Tecnai-F20 (200 kV) transition electron microscope equipped with a Gatan imaging filter (GIF) with an energy resolution of about 1.1 eV as measured in each experimental spectrum for the full-width at half-maximum (FWHM) of the zero loss peak. The EELS measurements were carried out in a conventional TEM diffraction mode with an approximately parallel beam of incident electrons. The crystals were tilted slightly off the zone axes by 1–2° to avoid the electron channeling effects close to the Bragg condition [12]. Orientation dependence in EELS arises basically from the anisotropic features of unoccupied electronic states [13,18]. So, in the MB_2 materials, the shape of the spectra in general depends markedly on the orientation of the specimen. Theoretical studies [3] have revealed that the key electronic states of MB_2 at E_F consist of the σ bonds (p_x+p_y) between the B atoms perpendicular to the c-axis and the π bonds (p_z) parallel to the c-axis. Therefore, the final states for B-K edge EELS spectra will mainly be the p_z states when the momentum transfer q is parallel to the c-axis and the p_x+p_y states when q is perpendicular to the c-axis. In order to probe the contribution of various p orbitals to the B-K edge spectra, we employed two different methods based on the proposal of Browning et al. [19]. First, we recorded the spectra in two orthogonal crystallographic orientations with a small collection semiangle keeping the momentum transfer q approximately parallel to the incident electron beam. We can therefore get the spectra corresponding specifically with final orbital states. Next, we collected a series of spectra by varying the collection semiangle in the same crystallographic orientation, which could give rise to a number of spectra depending on the collection angle, because according to the conservation of momentum, the direction of the momentum transfer q in inelastic scattering events will change rapidly from parallel to perpendicular to the incident electron beam with an increase of the collection semiangle. This latter method requires only one specimen for spectra acquisition instead of two specimens required by the original method, and consequently minimizes the influence of specimen individuality on the experimental results. In addition, the latter method combined with theoretical calculations for the relevant orientations also permits us to determine a good approximation of the "magic" angle [20].

3. Results and discussion

3.1. Electronic structure of NbB_2

We first calculated the electronic band structure and density of states (DOS) of NbB_2 using the LAPW method via Wien2k code [17]. Fig. 1 shows the total DOS and its decomposition onto the Nb and B atoms. It can be clearly recognized that the electronic states near the Fermi level (E_F) are mostly dominated by Nb 4d and B 2p states, and a minimum in the total DOS at around 1.85 eV below E_F (the so-called pseudogap [21]) separates the bonding and antibonding states. Hence, the in-plane B p−σ states from the sp^2 hybridization within the hexagonal B sheets are fully occupied, and the charge carriers in the present system are electrons in contrast to what has been observed in the well-known MgB_2 superconductor whose charge carriers are holes due to the partially occupied B p−σ states [3]. The peak at 12 eV below E_F is dominated by the B 2s states, and the broad peak at around 5 eV below E_F corresponds to the B 2p and Nb 4d states. Above the E_F, notable unoccupied states arise, respectively, from the niobium 4d states (~2.8 eV), the B p–π* (~5–6 eV), and the B p−σ* (~10–16 eV) states. These unoccupied states in principle can be well characterized by the orientation-dependent experimental EELS, as explained in the following sections.

The atom- and orbital decomposition of the total DOS, in Fig. 1(b), reveal apparent hybridization of the Nb 4d states with the B 2p states, particularly with the out-of-plane B p_z states due to the highly anisotropic structure. These facts suggest that the inter-layer interaction in NbB_2 is stronger than that in the MgB_2 superconductor. This feature is also indicated by the relatively smaller lattice parameter along the c-direction in NbB_2 with $c=0.330$ nm in comparison with $c=0.352$ nm for MgB_2 [2]. The strong hybridization between the Nb 4d states and the B 2p states, together with a remarkable charge transfer, could result in