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Soft-x-ray spectroscopy measurements of the *p*-like density of states of B in MgB_2 and evidence for surface boron oxides on exposed surfaces

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Soft-x-ray absorption and fluorescence measurements are reported for the *K* edge of B in MgB_2. The measurements confirm a high density of B $p_{xy}(\sigma)$ states at the Fermi edge and extending to approximately 0.9 eV above the edge. A strong resonance is observed in elastic scattering through a core exciton derived from out-of-plane $p_z(\pi^*)$ states. Another strong resonance, observed in both elastic and inelastic spectra, is identified as a product of surface boron oxides.

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Nagamatsu *et al.* have recently identified MgB_2 as a superconductor with a T_c of 39 K.[1] This readily available compound consists of hexagonal, graphitelike layers of boron separated by layers of Mg. The Mg is partially ionized, donating electrons to the boron layer. The extra electrons help stabilize the sp^2 bonding of the boron layer, but do not completely fill the band associated with the in-plane p_{xy}-bonding orbitals. The resulting high density of p_{xy} states at the Fermi level is believed to contribute to the high T_c of the compound.

Soft-x-ray absorption (SXA) and fluorescence (SXF) measurements at the B *K* edge provide ideal tools for directly measuring the density of the crucial boron *p* states in this compound. These spectroscopies involve dipole selected electronic transitions from and to a B 1*s* state, and thus provide a direct measure of the occupied and unoccupied *p*-like density of states of B in MgB_2. SXF is a filled-state spectroscopy that maps the states below the Fermi edge and SXA an empty-state spectroscopy mapping the states above the edge.[2] In this report we provide measurements of these spectra and compare the results with the calculated *p*-like partial density of states (PDOS) of boron in MgB_2. The measurements confirm the accuracy of standard band structure codes for MgB_2 and the existence of a high PDOS derived from the B p_{xy} orbitals at the Fermi edge.

Our measurements also indicate that surface oxides of boron are present in samples exposed to air so that careful protection of MgB_2 from ambient atmosphere may be required in applications. MgB_2 is relatively stable when exposed to air as is obvious from the very large volume of successful measurements that have been reported for powdered, sintered, and compressed samples. Nevertheless, it is known to be hygroscopic, and reported work has indicated the formation of Mg oxides and hydroxides at the surface.[3] We observe resonance features in both the SXA and SXF spectra that indicate that surface boron oxides are also formed.

The sample was synthesized at Oak Ridge National Laboratory in powdered form, pressed and sintered to a density of about 70%, and characterized with magnetization measurements. The measured T_c was 39 K.

In Figs. 1(a) and 1(b), we present the SXA absorption spectra of MgB_2 as measured by total fluorescent yield (TFY) and total electron yield (TEY) measurements, respec-

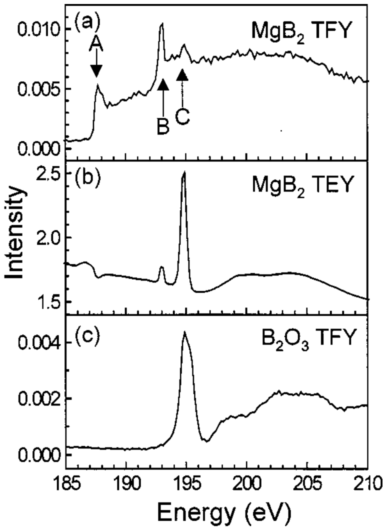

FIG. 1. (a) Total fluorescent yield of MgB_2 identifying three resonance features discussed in the text. (b) Total electron yield of MgB_2. (c) Total electron yield of B_2O_3 showing resonance at a peak coincident with peak *C* of curves (a) and (b).

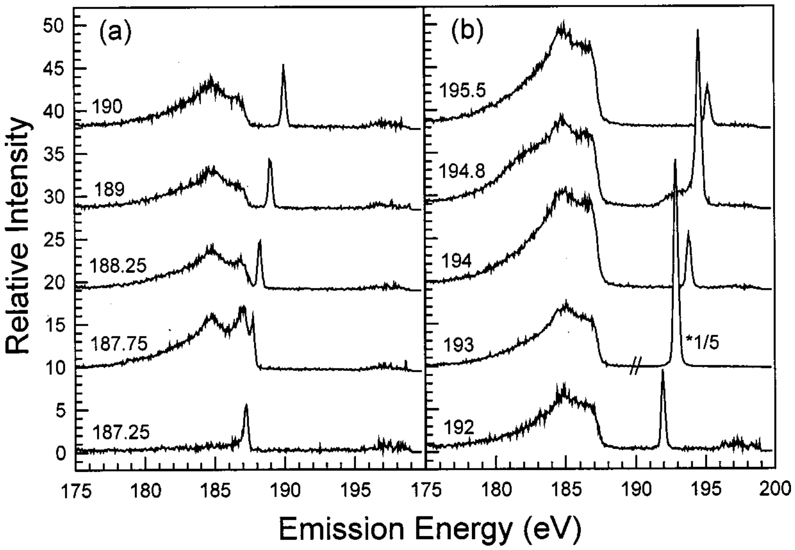

FIG. 2. SX fluorescence spectra excited near the boron *K* threshold. (b) SX fluorescence spectra excited near the core-exciton resonances for MgB_2 and boron oxide.

tively. Three peaks are noted in the TFY spectra that are of special interest. Peak *A* at the threshold is derived from the high, unfilled p_{xy}-PDOS extending above the Fermi level. Peak *B* is associated with a strong resonance in the elastic scattering rather than from inelastic scattering processes that contribute to the SXF spectra. As discussed further at the end of this paper, we believe that peak *C* is associated with resonantly enhanced elastic and inelastic scattering from boron oxides.

The TEY spectrum in Fig. 1(b) does not show a peak at the absorption threshold, but instead shows a shallow dip at the position of peak *A*. This is a result of the circumstances that the absorption threshold is superimposed on a strong background of electron emission from valence band electrons and the Mg *L* core levels, coupled with the competition of radiative and electronic deexcitation following the excitation of the B 1*s* core. Near threshold, SXF spectra are often dominated by a resonant inelastic x-ray scattering (RIXS) process[2] in which coupling of incident and emitted photons creates strong resonant photon emission. When this becomes the strongly dominant deexcitation channel, few TEY electrons are produced by excitation of the 1*s* electrons at the *K* edge, and electronic excitation of valence and shallow core levels is reduced, generating a net decrease in electron emission. Clearly, in this case, the resonant radiative deexcitation channel is dominant so that the TFY spectrum is the appropriate spectrum to use for measuring structure in the density of states just above the threshold.

Emission spectra excited in the threshold region are shown in Fig. 2(a) and in the region of the *B* and *C* resonances in Fig. 2(b). The sharp peaks with a width of about 0.4 eV are produced by elastic scattering of incident photons. Their widths provide a direct measure of the combined resolution of the beamline monochromator, which delivers incident photons, and the emission spectrometer, which detects emitted photons. Their presence in the emission spectra provides a very accurate method of comparing the energy scales of the beamline monochromator and emission spectrometer. The spectra located between about 180 and 188 eV are the normal emission spectra, which provide a measure of the filled-state *p*-PDOS of B in MgB_2. The resonant enhancement of the upper shoulder in the spectrum excited at 187.75 eV is clear evidence for the presence of the RIXS process in the threshold region. All of the emission spectra excited at energies above about 190 eV, and excepting those excited at the resonance energy *C*, are essentially identical and provide a reliable measure of the *p*-PDOS of filled states at the boron site in MgB_2.

In Fig. 3(a), we plot the SXF and near-threshold TFY absorption spectra together. The spectra overlap appropriately at the Fermi edge and provide a measure of the filled and empty *p*-like PDOS, modified primarily by instrumental broadening factors. We also plot [Fig. 3(b)] a theoretical

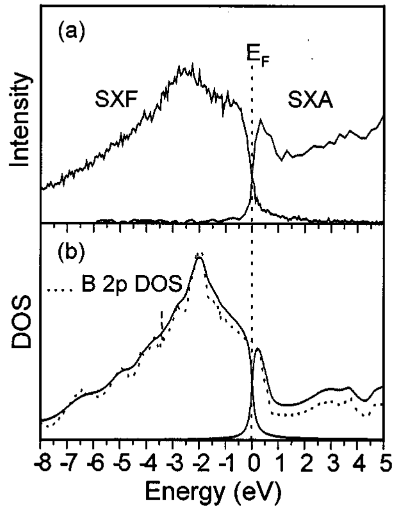

FIG. 3. Comparison of SX emission (SXF) and absorption (TFY) spectra with (b) calculated *p*-like partial density of states for boron in MgB_2. The solid curve is the theoretical curve (dotted) broadened by thermal, lifetime, and instrumental functions.

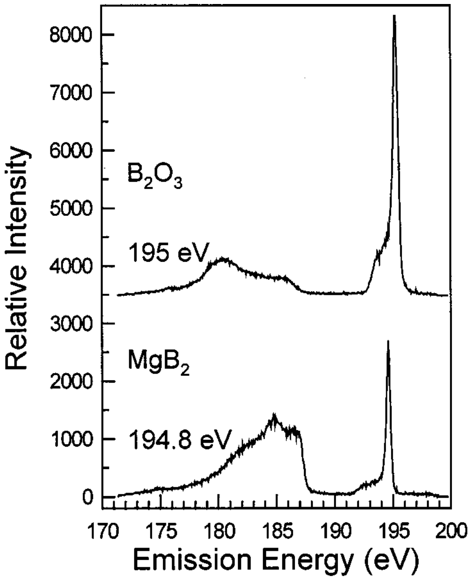

FIG. 4. Comparison of boron *K* spectrum of MgB_2 excited at the "oxide" resonance (lower curve) with on-resonance excitation of B_2O_3 (upper curve).

p-PDOS for B in MgB_2, calculated with the WIEN97 code.[4] Our band structure is indistinguishable from that of others obtained with the same code.[5] The dotted line in the theoretical curve is obtained from the code and the solid curve has been obtained by broadening the curve with instrumental resolution functions appropriate for the beamline monochromator and emission spectrometer. There is excellent general agreement between the experimental and theoretical curves. An analysis of the threshold peak in the absorption spectrum indicates that the p_{xy}-PDOS extends about 0.9 eV above the Fermi level.

In Fig. 2(b), the elastic peak is resonantly enhanced by a factor of 20 at 193 eV, the energy position of peak B of Fig. 1(a), while no change is observed in the emission spectrum. This results from elastic scattering through an intermediate core-exciton state derived from the localization of empty $p_z(\pi^*)$ orbitals. This resonant enhancement may be compared with the π^* resonance in hexagonal BN, where the intensity enhancement in the elastic peak is an order of magnitude greater than observed here.[6] The difference may be attributed to the circumstance that the exciton lies within the band gap of *h*-BN and overlaps conduction band states in MgB_2.

In Figs. 1(a) and 1(b), we note that peak *C* is strongly enhanced in the TEY spectrum as compared with the TFY. Since TEY measurements are far more surface sensitive than TFY measurements, this result is consistent with our interpretation of this peak as being associated with surface boron oxides. In Fig. 1(c), we plot the absorption spectrum of B_2O_3, which shows a strong resonance very close to the position of peak *C* in the MgB_2 sample, further supporting this interpretation of the peak.

The spectrum excited at 194.8 eV, the energy of *C* in Fig. 1, shows a moderate ($\times 4$) enhancement of the elastic peak, but also shows a low-energy shoulder on the elastic peak and a broad enhancement of the SXF spectra centered at about 182 eV. As shown in Fig. 4, both of these features are similar to features observed in the spectra of B_2O_3. Here, the MgB_2 spectrum excited at the *C* resonance is compared with the spectrum of B_2O_3 excited at its resonance peak. As a final test of the identification of peak *C* as being associated with boron oxide, we removed the sample from vacuum and left it in ambient air for 20 h rather than in a desiccator. When returned to vacuum and remeasured, peak *C* had doubled in relative magnitude when compared to peaks *A* and *B*. Finally, we note that the contribution of oxides to the observed spectra was significant only when enhanced by strong resonance effects and did not contribute significantly to the reported spectra at other energies.

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