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Polarization-dependent x-ray-absorption spectroscopy of $R\mathrm{Ni_2B_2C}$ ($R=\mathrm{Er}$ to Lu): Reduced Ni-$3d$ occupancy in $\mathrm{YbNi_2B_2C}$

Chandan Mazumdar,[1] Z. Hu,[2] H. von Lips,[2] M. S. Golden,[2] J. Fink,[2] P. C. Canfield,[3] and G. Kaindl[1]

[1]*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany*
[2]*Institute for Solid-State and Materials Research (IFW), Dresden, P.O. Box 270016, D-01171 Dresden, Germany*
[3]*Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011*
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We present here the results of polarization-dependent x-ray-absorption near-edge structure (XANES) studies at the B-K, C-K, and Ni-L_3 thresholds of single-crystalline borocarbide compounds $R\mathrm{Ni_2B_2C}$ (with $R=\mathrm{Er}$ to Lu) using bulk-sensitive fluorescence yield technique. The Ni-L_3 XANES spectrum for $\mathrm{YbNi_2B_2C}$ with photon polarization parallel to the ab plane is significantly more intense than in analogous spectra of other members of this series. This indicates a reduced Ni-$3d$ occupancy in the $\mathrm{Ni_2B_2}$ layer in $\mathrm{YbNi_2B_2C}$, a fact that might be responsible for the absence of superconductivity in this material.

The observation of superconductivity in the Y-Ni-B-C system ($T_C \approx 15$ K) (Refs. 1 and 2) and in the Y-Pd-B-C system ($T_C \approx 23$ K) (Ref. 3) has rekindled intense theoretical and experimental interest in intermetallic superconducting systems. While the Y-Pd-B-C material has not been synthesized so far in single-phase form, the superconducting Y-Ni-B-C phase has been identified as $\mathrm{YNi_2B_2C}$.[4] The structure of $\mathrm{YNi_2B_2C}$ is a filled variant of the tetragonal $\mathrm{ThCr_2Si_2}$ structure (space group $I4/mmm$) (Fig. 1, inset), which contains alternating layers of a rocksaltlike Y-C layer and $\mathrm{Ni_2B_2}$ arrays consisting of square-planar Ni layers sandwiched between boron planes giving a $\mathrm{NiB_4}$ tetrahedral form, with a gradual changing in B-Ni-B tetrahedral angle (angle made by a Ni-atom with two closest boron atoms which are along the c axis) from 102° for $\mathrm{LaNi_2B_2C}$ to 106° for $\mathrm{GdNi_2B_2C}$ to 108.8° for $\mathrm{LuNi_2B_2C}$.[5] The $R\mathrm{Ni_2B_2C}$ compounds ($R=\mathrm{Dy}$, Ho, Er, Tm, and Lu) exhibit an interplay between superconductivity and magnetism, and their superconducting transition temperatures (T_C) apparently scale with the deGennes factor.[6–9] Both band-structure calculations[10] and experimental observations[11] show that the electronic structure and transport properties of these superconducting compounds are three dimensional in character, despite their anisotropic crystal structure. The density of electronic states (DOS) at the Fermi level (E_F) in these systems is predicted to be nearly 50% of Ni-$3d$ character, with additional significant contributions from the B-$2p$, C-$2p$, and R-$5d$ states.[10] According to the deGennes scaling, $\mathrm{YbNi_2B_2C}$ was expected to show superconductivity at ≈ 12 K, but turned out to be nonsuperconducting down to 0.34 K.[12,13] Yb-L_3 x-ray-absorption near-edge structure (XANES) studies have shown that Yb ions are trivalent, like in all other rare-earth analogs, and do not change their valence with temperature.[12] From thermodynamic and transport measurements in polycrystalline $\mathrm{YbNi_2B_2C}$ (Ref. 12) and single-crystalline $\mathrm{Lu_{1-x}Yb_xNi_2B_2C}$ samples,[13,14] it was shown that in $\mathrm{YbNi_2B_2C}$, Yb ions strongly hybridize with those conduction electrons that give rise to superconductivity. It has been argued[14] that since the Kondo temperature of $\mathrm{YbNi_2B_2C}$ ($T_K \approx 10$ K) is of the same order of magnitude as T_C of $\mathrm{LuNi_2B_2C}$ ($T_C = 16.5$ K), an exceptionally enhanced pair breaking takes place in

$\mathrm{YbNi_2B_2C}$.[14] The pair breaking by Yb ions is so strong that even 10 at. % Yb in both $\mathrm{LuNi_2B_2C}$ and $\mathrm{YNi_2B_2C}$, suppresses T_C of the host compound by more than 12 K.[14,15] Because of this hybridizing nature of Yb ions in $\mathrm{YbNi_2B_2C}$, the exchange interaction and density of states change as well, leading to the failure of deGennes scaling in $\mathrm{YbNi_2B_2C}$.

As shown previously for the cuprates, it is possible to shed light on the origin of superconductivity by studying the normal-state electronic structure.[16] Polarization-dependent XANES is a powerful tool to explore the electronic structure and bonding character. Since in XANES the transitions from a core level are governed by the dipole selection rule, one
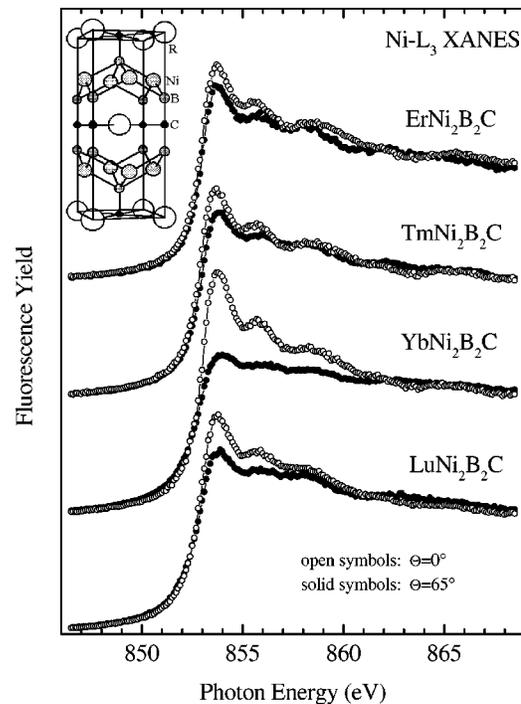

FIG. 1. Polarization-dependent Ni-L_3 XANES spectra of $R\mathrm{Ni_2B_2C}$ (with $R=\mathrm{Er}$, Tm, Yb, and Lu) taken with the polarization vector parallel to the ab plane ($\Theta=0°$: open symbols) and at an angle of $\Theta=65°$ relative to this plane (closed symbols). Inset: Crystal structure of $R\mathrm{Ni_2B_2C}$.

obtains information on the spatial distribution of the B-$2p$, C-$2p$, and Ni-$3d$ unoccupied states by measuring the polarization dependence of the XANES spectra at the K edges of boron and carbon ($1s \rightarrow 2p$) and at the L edges of nickel ($2p \rightarrow 3d/4s$). Since the probability for transitions from $2p$ to $4s$ states is about 30 times smaller than that from $2p$ to $3d$ states,[17] the experimental results basically reflect the nature of $3d$ unoccupied states. With single-crystal samples and linearly polarized photons, it is possible to selectively excite states with specific symmetries. In our case, when the polarization of the incident light is parallel to the ab plane ($E \| ab$), the transitions in the B-K and C-K XANES spectra take place only to final states with $2p_x$ (or $2p_y$) symmetry, and in the Ni-$L_{2,3}$ XANES spectra to states with $d_{x^2-y^2}$ or d_{xy} symmetry. When the polarization of the incident light is perpendicular to the ab plane ($E \| c$), the transitions in the B-K and C-K-XANES spectra take place only to $2p_z$ orbitals and in the Ni-$L_{2,3}$ XANES spectra to $3d_{z^2-r^2}$ orbitals. Thus, a systematic investigation of the distribution of the unoccupied electronic states, selected in terms of their symmetry, in the series RNi$_2$B$_2$C (R=Er to Lu) should help us understand the origin of the absence of superconductivity in YbNi$_2$B$_2$C.

To the best of our knowledge, XANES studies at the Ni-L_3 and B-K edges have been carried out so far only for polycrystalline RNi$_2$B$_2$C compounds (R=Y, Sm, Tb, Ho, Er, Tm, Lu),[18] where it was concluded that the unoccupied nickel and boron DOS close to E_F does not vary significantly for the various rare-earth elements, and hence cannot be correlated with the loss of superconductivity in the compounds with the lighter lanthanide elements. An electron-energy-loss spectroscopic (EELS) study of polycrystalline YNi$_2$B$_2$C has provided some additional information on the C-$1s$ excitation spectrum.[19] However, polarization-dependent XANES studies at the B-K, C-K, and Ni-L_3 edges have been carried out only recently, and only on single-crystalline YNi$_2$B$_2$C.[20] Here, we present the results of a systematic polarization-dependent XANES study on single-crystalline RNi$_2$B$_2$C compounds (with R=Er to Lu). We note that though in $4f$ hybridized systems, such as YbNi$_2$B$_2$C studied here, the effect of hybridization on the electronic state of the transition metal is very important, most of the XANES studies of such systems are confined to that of rare-earth ions. The present study is one of a few[21] which investigates XANES of the transition metal.

Single crystals of these materials were grown by the high-temperature Ni$_2$B flux method.[22] The platelike crystals were about 2 mm × 2 mm × 0.5 mm in size, and had surfaces corresponding to the ab planes. The lattice parameters of all crystals agreed well with literature values.[5] The polarization-dependent XANES studies were carried out at room temperature at the plane-grating-monochromator beamline SX700/II,[23] operated by Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). Due to the hardness of the studied materials, cleaving of the samples parallel to the ab planes in the measuring chamber is quite difficult;[24] hence the spectra were measured via the bulk-sensitive fluorescence-yield (FY)

method, which leads to a typical sampling depth of 1000 Å. The pressure in the experimental chamber was better than 5×10^{-10} mbar during the measurements. The sample holder was aligned to an accuracy of $\pm 2°$ by reflecting the zero-order incident beam. The energy resolution of the monochromator was set to around 250 meV, 200 meV, and 600 meV at the B-K, C-K, and Ni-L_3 absorption edges, respectively. The monochromator energy was calibrated by measuring the Cu-L_3 and O-K edges of CuO. To avoid effects of variations of the photon flux with time, the spectra thus obtained were divided by the beam flux monitored simultaneously. An energy-dependent structure in the photon flux, which is particularly strong near the carbon K edge, was corrected by measuring the total-electron-yield (TEY) spectra of a clean gold foil that was cleaned *in situ* with a diamond file, and dividing the FY spectra of the sample by the TEY spectra of the gold foil measured in the same energy range. All these spectra were then corrected for self-absorption using the procedure described by Tröger *et al.*[25] The spectra at all three edges measured here, were normalized at an energy of about 80 eV above the absorption edge, where the final states are essentially isotropic.

The Ni-L_3 XANES spectra of RNi$_2$B$_2$C are shown in Fig. 1. In cases of LuNi$_2$B$_2$C, TmNi$_2$B$_2$C, and ErNi$_2$B$_2$C, the spectra taken at normal incidence ($\Theta = 0°$: open symbols, where Θ is the angle between the polarization vector and the surface) are only slightly more intense than those taken at grazing angle ($\Theta = 65°$: closed symbols); this indicates that the anisotropy of the distribution of Ni-$3d$ states is only minor. It is to be noted that if there would be saturation effects, which are more pronounced at grazing angle, the observed difference in intensities for the two configurations could be explained. However, one also has to note that any such saturation effect would remain the same for all compounds studied, and hence a relative comparison of the spectra taken for the various compounds is valid. Considering that on closer examination one notices that the difference between the intensities at the Ni-L_3 edges, taken at normal and grazing incidence, decreases discernibly and systematically with decreasing atomic number of the lanthanide element, there seems to be a genuine effect of anisotropy, even though small. This anisotropy is related to the difference of the partial density of states projected on the ab plane or perpendicular to it. This small anisotropic distribution of Ni-$3d$ states may be a consequence of the distortion of the NiB$_4$ tetrahedra, where the distortion depends on the size of the lanthanide atom.[5]

In the case of YbNi$_2$B$_2$C, a much more intense peak is observed at the Ni-L_3 absorption edge in the $\Theta = 0$ spectrum. One can also note that though the $\Theta = 65°$ spectrum exhibits a slightly reduced intensity in YbNi$_2$B$_2$C than their counterparts in other compounds measured here, it is not true that the location of empty states has just moved from the c axis to the ab plane. The sum of the intensities of the peak parallel and perpendicular to the ab plane in YbNi$_2$B$_2$C are clearly larger than those measured for other members of this series. This indicates a reduced Ni-$3d$ occupancy in the in-plane states of YbNi$_2$B$_2$C. Since superconductivity in this family of materials is believed to arise from Ni-$3d$ electrons,
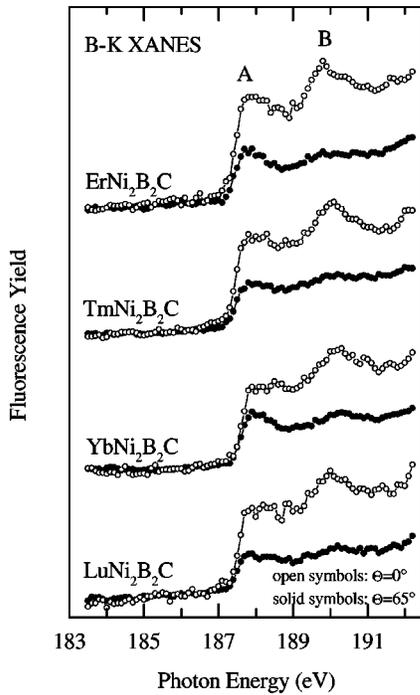
FIG. 2. Polarization-dependent B-K XANES spectra of RNi$_2$B$_2$C (with R = Er, Tm, Yb, and Lu) taken with the polarization vector parallel to the ab plane ($\Theta = 0°$: open symbols) and at an angle of $\Theta = 65°$ relative to this plane (closed symbols).

FIG. 3. Comparison of polarization-dependent Ni-L_3, B-K, and C-K XANES spectra of YbNi$_2$B$_2$C and LuNi$_2$B$_2$C, measured with the polarization vector parallel to the ab plane ($\Theta = 0°$: open symbols) and at an angle of $\Theta = 65°$ relative to this plane (closed symbols). The spectra were aligned at their respective absorption thresholds.

this result seems to give direct evidence as to why superconductivity should be absent in YbNi$_2$B$_2$C. We would like to point out that this difference is no longer observed when the total number of $3d$-valence electrons is reduced by replacing Ni, e.g., by Co. In the case of nonsuperconducting Y(Ni$_{0.7}$Co$_{0.3}$)$_2$B$_2$C, e.g., though the total number of $3d$ electrons is diluted by substitution with Co, no change in the $3d$ states is found from Ni-L_3 XANES spectra.[20] Since it was earlier shown from thermodynamic and transport properties measurements[12–14] that Yb ions hybridize much stronger than other rare earths in this series of compounds, we believe that the reduced $3d$ occupancy deduced from observations is directly related to the effects of hybridization on the Ni-$3d$ states, and not merely due to a reduction in the number of valence electrons in YbNi$_2$B$_2$C. This suggests that it is the cause for suppression of superconductivity in YbNi$_2$B$_2$C. While the known systematic from structural data from powder samples suggests that there is no drastic change in the NiB$_4$ tetrahedron of YbNi$_2$B$_2$C,[5] in view of the importance of the material, a conformation of the same is desirable from a structural study with a single-crystal sample of the material.

The B-K edge XANES spectra of RNi$_2$B$_2$C are shown in Fig. 2. It should be pointed out that unlike the case of FY measurements at the Ni-$L_{2,3}$ absorption thresholds, the FY at the K threshold of the light elements boron and carbon is rather weak and difficult to detect. In this work, we overcame this problem by using a windowless Ge fluorescence detector maintained in very clean and ice-free conditions. Unlike the case found at the Ni-L_3 edge, a prominent anisotropic behavior of the B-K XANES spectra (Fig. 2) is seen in all com-
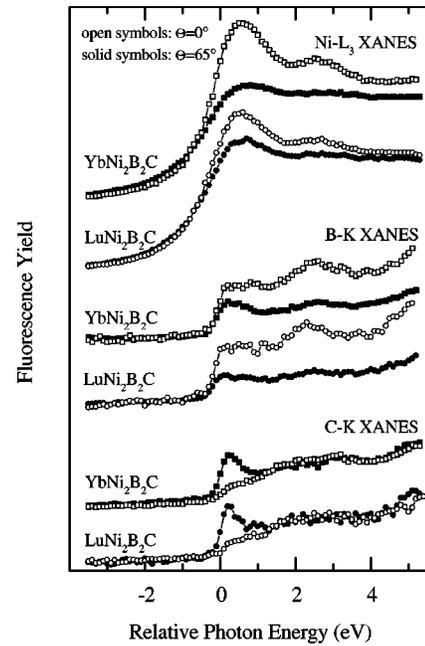
pounds studied here. The spectral intensity is stronger when the plane of polarization is parallel to the sample surface, indicating a higher degree of unoccupied $2p_x$ (or $2p_y$) states in the Ni$_2$B$_2$ plane as compared to $2p_z$ states. The observed features are qualitatively similar to those observed as well as calculated [by the local-density approximation (LDA) method] for the B-K edge of single-crystalline YNi$_2$B$_2$C.[20] There is a small but systematic variation, depending on the rare-earth element, in peak A (Fig. 2) which may arise from the slight change in the NiB$_4$ tetrahedron,[5] as also suggested from the results of Ni-L_3 XANES spectra. The anisotropy in peak A in B-K edge spectra of YbNi$_2$B$_2$C is the smallest. Whether anisotropy being smallest for YbNii$_2$B$_2$C is because of a component arising from hybridization of $4f$ electrons, directly or via Ni, is not clear at present.

The C-K edge spectra of Lu and Yb compounds are shown in Fig. 3 as part of an overall comparison of the Ni-L_3, B-K, and C-K spectra. For the purpose of comparison, the spectra were redrawn with respect to the energies of the absorption thresholds (187.7 eV for B-K, 281.6 eV for C-K, and 853.2 eV for Ni-L_3). Both in the Lu and Yb C-K XANES spectra, we observe an anisotropy, but unlike the case of the XANES spectra taken at the Ni and B edges, the anisotropy is confined to the threshold region only. A sharp peak is observed in the $\Theta = 65°$ spectrum, but only a shallow step is found in the $\Theta = 0°$ spectra. The spectral intensity of the $\Theta = 65°$ C-K edge spectrum is higher than that of the $\Theta = 0°$ spectrum, whereas the reverse is true for Ni-L_3 and B-K edge spectra. No perceptible difference is seen between the Lu and Yb spectra. From the crystal structure, we realize

that the boron and carbon atoms are situated approximately one over the other in two different planes (see Fig. 1, inset). This suggests that the sharp peak immediately above the absorption threshold originates from hybridization of B-$2p_z$ and C-$2p_z$ orbitals. At the energy 1 eV above threshold, the C-K XANES spectra exhibit a relatively small anisotropy as compared to the B-K XANES spectra, and are also significantly different from those in YNi$_2$B$_2$C observed previously.[20] It is surprising to note that though the local environments of both B and C atoms are anisotropic, yet C-K edge spectra exhibit an essentially isotropic character except for a small range at the threshold energy.

From an overall comparison of Ni-L_3 and B-K spectra (Fig. 3), a hybridization between B-$2p$ and Ni-$3d$ orbitals is evident, suggesting covalency of the Ni-B bond. In both cases, the energy positions of the XANES structures nearly match. Since the nickel and boron atoms are located approximately in the same plane in this crystal structure, the hybridization in the plane should be stronger, as evidenced by the more pronounced structures in the B-K and Ni-L_3 XANES spectra taken for $\Theta = 0°$ as compared to $\Theta = 65°$. A similar feature was also observed earlier by Pellegrin *et al.* in a study of polycrystalline compounds.[18]

In conclusion, we have studied the unoccupied B-$2p$, C-$2p$, and Ni-$3d$ density of states of single-crystalline RNi$_2$B$_2$C ($R =$ Er to Lu) by measuring polarization-dependent XANES spectra. The results demonstrate the potential of polarization-dependent measurements of single-crystalline samples. Our results indicate a weakly anisotropic Ni-$3d$ and strongly anisotropic B-$2p$ unoccupied density of states for all compounds studied. The anisotropy in the unoccupied C-$2p$ density of states is confined only to the threshold region. A higher spectral intensity of the Ni-L_3 XANES peak close to absorption threshold for YbNi$_2$B$_2$C is observed as compared to other members of this series. We argue that this reduction in the occupancy of the Ni-$3d$ states is the result of hybridization, which in turn is the cause of that suppression of superconductivity in YbNi$_2$B$_2$C.

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