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CORE ELECTRON SPECTROSCOPIC STUDIES OF $\text{YNi}_2\text{B}_2\text{C}$

T. Böske, M. Kielwein, M. Knupfer, S. R. Barman,¹ G. Behr, M. Buchgeister, M. S. Golden and J. Fink
Institut für Festkörperforschung, IFW Dresden e.V. Postfach 270016, D-01171 Dresden, Germany

D. J. Singh and W. E. Pickett

Complex Systems Theory Branch, Naval Research Laboratory, Washington, DC 20375, U.S.A.

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High-energy electron energy-loss spectroscopy in transmission has been applied to obtain the absorption spectra at the B 1s, C 1s and Ni $2p_{3/2}$ excitation edges of bulk polycrystalline $\text{YNi}_2\text{B}_2\text{C}$. We find a close similarity in the near-edge structures and confirm the strongly covalent character of the bonding between Ni, B and C. We compare our results to band structure calculations of the local unoccupied density of states generated within the local density approximation. From x-ray photoemission spectroscopy measurements we determine the core level binding energies and from a comparison of photoemission and Auger spectroscopic measurements we derive a value of the Ni d-d Coulomb energy U_A of about 4eV. Copyright © 1996 Published by Elsevier Science Ltd

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THE DISCOVERY of a rather high superconducting transition temperature (T_c) of up to 23K in some quaternary intermetallic compounds containing rare-earth (RE) and transition metals in 1994 [1, 2] has given rise to the question, whether the superconductivity in these compounds can be described within a BCS-scenario [3] or whether models based on a correlated electronic structure [4] such as in the high- T_c cuprates are more appropriate. The crystal structure of RE- $\text{Ni}_2\text{B}_2\text{C}$ seems to point to the latter, since the Ni_2B_2 structural units form a two-dimensional layer comparable to the CuO_2 planes in the cuprates [5]. Band structure calculations generated within the local density approximation (LDA) have been performed on different borocarbides [6–8], all predicting that the electronic structure is dominated by strongly covalent bonding between the constituent atoms and thus is clearly three-dimensional. This appears to be in contrast to the cuprates, whose electronic structure is believed to be defined by the correlated two-dimensional electronic states in the CuO_2 planes. The electronic structure of RE- $\text{Ni}_2\text{B}_2\text{C}$ has been studied experimen-

tally so far using resonant photoemission (RESPES) [9, 10], bremsstrahlung isochromat spectroscopy (BIS) [9], angle-resolved photoemission (ARPES) [11] and x-ray absorption spectroscopy (XAS) [12]. In this paper, we report investigations of $\text{YNi}_2\text{B}_2\text{C}$ using both high-energy electron energy-loss spectroscopy (EELS) in transmission and x-ray photoelectron spectroscopy (XPS).

The polycrystalline $\text{YNi}_2\text{B}_2\text{C}$ samples were produced by arc-melting following the recipe of Cava *et al.* [2]. Phase purity and chemical composition were checked with x-ray diffraction and scanning electron microscopy. Secondary phases are present, but amount to less than 5%. More details on the sample preparation can be found elsewhere [13]. The desired thin films for the EELS experiments were cut from a $\text{YNi}_2\text{B}_2\text{C}$ pellet, using an ultra-microtome equipped with a diamond knife and then mounted on a standard electron-microscopy grid. The film thickness was about 1500Å. The phase-purity after cutting was checked additionally in the energy-loss spectrometer by Bragg scattering.

The 170keV transmission electron energy-loss spectrometer is described in detail elsewhere [14]. We emphasise that EELS in transmission is a bulk sensitive

¹ On leave from: Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, 560012 India

method, in contrast to XAS recorded in electron-yield mode whose depth scale is restricted to the sample surface due to the small electron mean-free path at lower kinetic energies. The energy resolution of the spectrometer was set to 0.4 eV at the $\text{Ni } 2p_{3/2}$ and 0.16 eV at the $\text{B } 1s$ and $\text{C } 1s$ absorption edges, respectively. In all cases the momentum transfer resolution was $0.2 \text{ \AA}^{-1}$ and the spectra were recorded in forward direction.

The XPS measurements were performed using a commercial spectrometer [15] with unmonochromatised $\text{Al-K}\alpha$ radiation. The energy calibration of the spectrometer was checked prior to and after the measurements using the $\text{Au } 4f$, $\text{Ag } 3d$ and $\text{Cu } 2p$ standard photoemission lines of the metallic elements. The total experimental resolution was estimated to be about 0.9–1.0 eV using the full width at half maximum (FWHM) of the $\text{Ag } 3d_{5/2}$ and $\text{Au } 4f_{7/2}$ photoemission lines. Prior to measurement, the borocarbide samples were scraped with a diamond file in situ at room temperature. For comparison, a sample of Ni metal was measured which was cleaned by sputtering with Ar ions. Sample cleanliness was monitored in each case by checking the $\text{O } 1s$ and $\text{C } 1s$ signals. The $\text{C } 1s$ binding energy of the carbide is well separated from the carbon contamination which shows a peak at about 285.5 eV. The Ni metal was atomically clean, whereas in $\text{YNi}_2\text{B}_2\text{C}$ small contamination with both oxygen and carbon were observed, independent of how much material was scraped off. We assume that the oxygen and carbon containing contamination is located at grain-boundaries. We checked carefully that the spectral features of all the other core levels were independent of the intensity of the $\text{O } 1s$ signal. Oxygen contamination was not observed in EELS, because of the bulk-sensitivity of this technique.

LDA calculations of the band structure and projected density of states (DOS) were performed using a local orbital extension of the full potential linearised augmented planewave (LAPW) method [16]. A well convergent basis of approximately 1060 LAPW functions was employed. Additional local orbitals were used for semicore states and to relax linearisation errors, as is necessary in calculating over a wide energy range as done here. 84 special k points in the irreducible wedge were employed during the iteration to self-consistency, while 288 points in the wedge were used for the calculation of the DOS and Fermi energy. Since the dipole selection rules hold for EELS at low momentum-transfer, we used Ni d-, B p- and C p-projected partial DOS. In case of the transition $\text{Ni } 2p \rightarrow (3d, 4s)$ the s partial DOS can be neglected due to the comparatively low value of the $2p \rightarrow s$ transition matrix element. Instrumental resolution and quasi-

Fig. 1. Energy-loss spectra at the $\text{Ni } 2p_{3/2}$, $\text{B } 1s$ and $\text{C } 1s$ excitation edges (dots) and calculated partial density of electronic states (solid line) broadened by experimental resolution and lifetime effects (see text for details).

particle lifetime broadening have been taken into account by convolution of the DOS functions of the unoccupied electronic states both with a Gaussian of FWHM equal to the experimental resolution and with a Lorentzian of FWHM according to $0.2 * (E - E_0)$, where E_0 denotes the zero point of the energy scale [9]. The effects of core hole lifetime broadening have also been included by convoluting the DOS functions with Lorentzians of FWHM of 0.4 eV in case of $\text{Ni } 2p_{3/2}$ and 0.2 eV in case of $\text{B } 1s$ and $\text{C } 1s$ [17]. Finally, the DOS functions have been normalised to the integrated intensity of the experimental energy-loss spectra in their common energy range.

Figure 1 contains the energy-loss spectra of $\text{Ni } 2p_{3/2}$, $\text{B } 1s$ and $\text{C } 1s$. A background curve has been subtracted from the experimental data which results in flat pre-edge regions except in case of the $\text{B } 1s$ edge, where small deviations due to extended fine-structures of the Y 3d absorption edges located at about 155 eV can be observed. The energy scale of Fig. 1 has been set to the inflection point of the rising edge in each case,

Table 1. EELS and XPS binding energies of selected core levels in $\text{YNi}_2\text{B}_2\text{C}$ and in Ni metal. XPS energies are given within $\pm 0.1\text{eV}$. In the case of EELS, the binding energies were obtained from the inflection point of the rising edge. For details see the text.

	EELS E_B (eV)	XPS E_B (eV)
Ni $3p_{3/2}$	—	67.0
Ni $3s$	—	111.3
Ni $2p_{3/2}$	853.2	853.4
Y $3d_{5/2}$	—	156.0
B $1s$	187.9	188.0
C $1s$	282.1	282.3
Ni metal $3p_{3/2}$	—	66.3
Ni metal $3s$	—	110.8
Ni metal $2p_{3/2}$	—	852.8

the actual energy of which we refer to as the EELS binding energy. Table 1 contains these EELS binding energies, together with the values obtained from XPS. We note that there is a rather strong chemical shift of the Ni $2p_{3/2}$ XPS core level with respect to the metal of about 0.6eV , and that the XPS binding energies of the Y core levels are very close to their values in the charge-neutral metal (the binding energy of Y $3d_{5/2}$ is given in Table 1) [18]. The C $1s$ and B $1s$ XPS binding energies are typical of the carbides [18] and the borides [19], respectively. In the following we will discuss the energy-loss spectra first and compare the structures to DOS calculations, then we will consider the x-ray photoemission spectra of the Ni core levels.

As can be seen in Fig. 1, most of the structures in the electron energy-loss spectra appear at approximately the same relative positions for all the core levels, showing the strong covalent character of the bonding between Ni, B and C. We conclude that the electronic structure of $\text{YNi}_2\text{B}_2\text{C}$ is essentially three-dimensional. We remark that a study of Ni and B core excitations alone [12] can only demonstrate the covalence within the Ni-B layers; since C is included here the full three-dimensional character of the bonding is shown. The Ni $2p_{3/2}$ leading edge appears to be considerably broader than the B $1s$ and C $1s$ edges, even after taking the different resolution into account, and there is a shift of the Ni $2p_{3/2}$ absorption maximum, compared to the analogous features in the B and C $1s$ spectra close to the Fermi edge, of about 0.3eV towards higher energy. Comparing our B $1s$ spectrum with that obtained by Pellegrin *et al.* [12], we recognise some differences: in particular the narrower peaks evident in this work, which reflect the superior energy resolution in EELS; and most notably a different position and shape of the structure at about 6eV above the onset, which we attribute to the bulk sensitivity of our method.

Also shown in Fig. 1 are the calculated broadened

DOS. The calculated Fermi energy (E_F) has been aligned to the zero point of the energy scale. The total DOS at and close to E_F are mostly due to d-like states of the Ni $3d$ -C $2s2p$ -B $2s2p$ hybrid, whereas p-like states from B and C contribute to the following DOS features up to $\sim 5\text{eV}$ with nearly the same weight as the d-like states. The DOS at $\sim 6\text{eV}$ is dominated by p-like states from the hybrid. There is a good match between the calculated partial DOS and the energy-loss spectra in Fig. 1, with the best agreement with respect to both the energy position and relative intensities of the features attained for the B $1s$ spectrum. For C $1s$, the position of the calculated DOS features occur at nearly the same position as the peaks in the energy-loss spectrum. The calculated intensity at the Fermi edge, however, is much higher than observed in the experiment; the reason for this is at present unclear. For Ni, the calculated structures seem to be shifted to lower energies. In particular between the calculated and the observed Ni $2p_{3/2}$ absorption maximum we note a difference of about 0.3eV . In addition, the Ni $2p_{3/2}$ absorption intensity at the Fermi edge appears to be smaller than in the calculated spectrum. Similar results have been obtained using XAS [12] and BIS [9], where the difference between the calculation and the experiment have been discussed in terms of spectral weight transfer from E_F to higher energies. It has been speculated, as to whether this transfer might be due to strong electron-phonon coupling effects [9], or due to effects of $3d$ electron correlation [12].

One possible way to obtain information on correlation effects and screening mechanisms in Ni is to apply core level photoemission, where the Ni core level satellite position is related to the $2p$ - $3d$ Coulomb interaction Q and a charge-transfer or transfer energy Δ , as has been demonstrated e.g. in insulating Ni dihalides [20] and Ni metal [21]. We have examined both $\text{YNi}_2\text{B}_2\text{C}$ and, for comparison, Ni metal with XPS to obtain the core and valence band satellite positions. In Fig. 2 the x-ray photoemission spectra of Ni $2p_{3/2}$, $3p_{3/2}$, and $3s$ in Ni metal and in $\text{YNi}_2\text{B}_2\text{C}$ are shown. The spectra have been aligned to the positions of the main peak, the XPS binding energies being listed in Table 1. Corrections have both been made of extrinsic energy losses using integral background subtraction [22] and for the x-ray satellite features. The Ni metal photoemission spectra show the familiar core satellite at about 6eV higher binding energy, assigned to be a $2p^53d^9$ final state, whereas the main line is due to the well-screened $2p^53d^{10}$ final state [21] (except in case of the Ni $3p$ doublet where the main peak seems to be composed of $3d^9$ and $3d^{10}$ final states [23]). The spectra of $\text{YNi}_2\text{B}_2\text{C}$ display a considerably weaker satellite at

Fig. 2. X-ray photoemission spectra of the Ni $2p_{3/2}$, $3p_{1/2,3/2}$ and $3s$ core levels of $\text{YNi}_2\text{B}_2\text{C}$ (dots) and in Ni metal (solid line). The zero point of the energy scale has been set to the maximum intensity for each spectrum, the actual binding energies are listed in Table 1. The inset shows the Ni L_3VV Auger spectrum (dots) and the self convoluted valence band spectrum (solid line). The Auger spectrum is plotted on a two-hole energy scale, whose zero is given by the Ni $2p_{3/2}$ XPS binding energy.

about 7.5 eV higher binding energy and are otherwise very similar to the spectra of Ni metal. In particular, no multiplet structure can be detected. We assume that in $\text{YNi}_2\text{B}_2\text{C}$ the same final state assignment as in Ni can be made. This proposal is supported by the comparison of EELS [24] and XAS [12] results of the Ni $2p$ absorption edges in $\text{YNi}_2\text{B}_2\text{C}$, in Ni metal and NiO: the integrated Ni $2p$ absorption signal in $\text{YNi}_2\text{B}_2\text{C}$ is nearly equal to that of Ni metal and about half of that of NiO, suggesting an approximate 3d occupancy of Ni metal of about 9.4.

To obtain information on the 3d–3d Coulomb interaction U , one can compare the self-convolution of the valence band photoemission spectrum with the L_3VV Auger transition [25, 26], which involves the decay of a $2p_{3/2}$ core electron and two valence 3d electrons. As-

suming the valence band satellite to be a $3d^8$ two hole state and the main line to be $3d^9$ as in Ni metal, the comparison should give information on U , because the Auger process can lead to a two-hole final state $3d^8$ in which the holes are located at the same site as in the satellite, whereas the self convolution of the main $3d^9$ valence band peak corresponds to two independent holes on different sites [25]. The zero point of the energy scale of the Auger spectrum is given by the Ni $2p_{3/2}$ binding energy. Both a constant and an integral background [22] have been subtracted from the spectra. The resulting Auger spectrum is displayed in the inset of Fig. 2. Also shown is the self-convolution of the valence band spectrum. The maximum of the Auger spectrum is assigned to the ^1G multiplet of the d^8 configuration, whereas the structures at lower energy are related mainly to the ^3F multiplet and at higher energy to the ^1S multiplet [26]. The maximum of the Auger spectrum occurs at about 8 eV at the position of the valence band satellite seen in RESPEC [9, 10]. The difference, U_A , between the peak maxima of the Auger spectrum and the self-convoluted valence band spectrum is attributed to the on site 3d–3d interaction. For this energy difference we obtain $U_A = 4.4 \pm 0.3$ eV; thus earlier derived estimates [9, 10] are found to be in fair agreement with this measurement. This value for U_A is approximate in the sense that the centre of gravity of the d^8 multiplet should be used in determining U . But since the ^1G multiplet dominates the Auger spectrum, this would introduce only small errors.

There are theoretical considerations [4] that $\text{YNi}_2\text{B}_2\text{C}$ is a two-dimensional, highly correlated system due to a large number of holes in the 3d shell. These considerations are connected with the existence of a trivalent Y ion. Our measurements contradict these models in so far, as the EELS results indicate a small hole-count in the 3d shell and a three-dimensional electronic structure, as follows also from our band structure calculations. From XPS we can deduce that Y is metallic rather than ionic. Moreover, from a comparison of XPS and Auger spectroscopy we deduce a value for U of about 4 eV which is still smaller than the valence band width of about 6 eV. These findings indicate that correlation effects are probably less important in $\text{YNi}_2\text{B}_2\text{C}$ than in the cuprates.

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