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The Electronic Structure of Intermetallic Borocarbide and Related Superconductors from High Energy Spectroscopy

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Photoemission has been applied to study the electronic structure of YNi_2B_2C and related materials, with comparison of the results with the density of states generated from band structure calculations. The absence in photoemission of the predicted peak in the density of states at the Fermi level in undoped YNi_2B_2C , and the inconsistency of the photoemission data with a rigid-band model for the effects of Co doping on the electronic structure of $YNi_{2-x}Co_xB_2C$ are discussed. In addition, recent photoemission data from the new superconductor $La_3Ni_2B_2N_3$ are presented.

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In the last two years, superconducting quaternary rare-earth or yttrium boro-carbides $RENi_2B_2C$ (RE = rare earths or Y) with T_C 's of up to 17K have been the subject of increasing research interest. In this contribution, we approach these new materials from the standpoint of their electronic structure - both as measured using high energy spectroscopy such as photoemission (PES) as well as from band structure calculations. In

the following, after summarizing the current status as regards the undoped borocarbide superconductors we consider the case in which Ni is partially replaced by Co. Lastly, we present x-ray photoemission (XPS) data from polycrystalline samples of the new boronitride material, $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_{3-\delta}$.

The polycrystalline $\text{RE-Ni}_{2-x}\text{Co}_x\text{B}_2\text{C}$ samples were prepared following the procedure given by Cava *et al.*¹ The phase purity and chemical composition were checked with x-ray diffraction and scanning electron microscopy. Secondary phases were present, but in each case amounted to less than 5%. Details of the sample preparation can be found in [2]. The boronitride samples were synthesised as is described in [3], resulting in material of high phase purity, whose x-ray diffractograms could be fully indexed adopting the crystal structure of $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_{3-\delta}$ given in [4]. The photoemission data presented here were recorded either at beamline 4.1 of the Surface Science IRC at the SRS, Daresbury Laboratory or using two commercial laboratory spectrometers, one equipped with a monochromatic $\text{AlK}\alpha$ source and the other a He discharge lamp. As photoemission is a surface sensitive technique, the samples were repeatedly scraped prior to measurement inside the ultrahigh vacuum chamber using a diamond file. This results in the production of a relatively clean surface provided the grain boundaries of the material are clean. A residual carbon contamination is always present, as demonstrated by the observed C1s XPS signal at binding energies (BE) corresponding to those of adventitious carbon at ($\sim 285\text{eV}$) in both the borocarbide (in which the carbide carbon is centred at $\text{BE}=282.3\text{eV}$) and boronitride samples. Calculations of the band structure and projected density of electronic states (DOS, $N(E)$) were performed within the local density approximation (LDA) to density functional theory using a local orbital extension of the full potential linearised augmented plane wave (LAPW) method.⁵ Further details of the calculation method and its comparison to high energy spectroscopic data are to be found in [6] and [7] respectively.

Fig. 1 shows a comparison between the valence band photoemission profile of $\text{YNi}_2\text{B}_2\text{C}$ recorded at 30K using He I radiation ($h\nu=21.22\text{eV}$) and the simulated PES spectrum. The simulation results from the appropriately weighted partial DOS for each atomic orbital which have been multiplied by their respective photoionisation cross-sections.⁸ The resultant simulated spectra are then convoluted with an energy-dependent Lorentzian to take lifetime broadening into account, and a Gaussian (60meV for Fig. 1) representing the experimental energy resolution (for details see Ref.[7]).

As can be seen from Fig. 1, the bandstructure calculations predict that there should be a peak in the PES spectrum at the Fermi level (E_F), the dominating contribution to which comes from Ni3d states.⁹ In contrast to this prediction, however, no peak is observed in the photoemission spectrum at E_F , and there appears to be a transfer of spectral weight away from the Fermi level to higher energies.^{7,10}

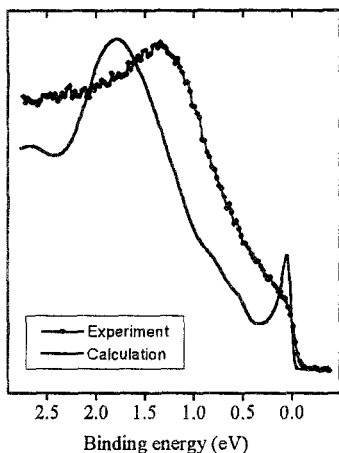


Fig.1. Comparison of the experimental [$h\nu=21.22\text{eV}$] and calculated photoemission spectra of $\text{YNi}_2\text{B}_2\text{C}$. The spectra are normalised to have equal intensity in their common energy range.

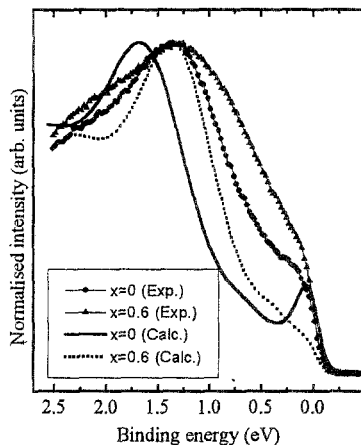


Fig.2. Comparison of the measured [$h\nu=40\text{eV}$, 'Exp.'] and calculated ('Calc.') photoemission spectra of $\text{YNi}_{2-x}\text{Co}_x\text{B}_2\text{C}$ ($x=0, 0.6$). The spectra are normalised to have equal maximum intensity.

The effects of electron correlation have been suggested to be responsible for the discrepancies seen in Fig. 1. For example, correlation in the borocarbides makes itself felt in the presence of a characteristic two-hole final state satellite in valence band photoemission spectra.^{7,10} However, a value of $U_{dd} \sim 4\text{eV}$ for $\text{YNi}_2\text{B}_2\text{C}$ has been determined from the comparison of Auger and valence band photoemission spectra.¹¹ Thus U_{dd} in $\text{YNi}_2\text{B}_2\text{C}$ is smaller than the Ni3d bandwidth ($\sim 6\text{eV}$) and in addition, as the bands near E_F are well away from half-filling, one would expect correlation effects to play less of a role here than in the high- T_c superconductors. Another opportunity to test the form of the DOS around E_F is presented by doping studies. In this case, it is possible to substitute Co for Ni, thus reducing the total electron density in the system. The idea here is that the band structure remains unaltered by the doping, which

merely causes a downward shift of the Fermi level. The predicted position of E_F in the bandstructure is such that a 'rigid-band' shift would result in a decrease of $N(E_F)$ upon Co-doping. This rigid-band approximation may well be justifiable in the case of moderate Co-substitution as the lattice parameters $a(c)$ decrease by only 0.03(0.19)% upon doping to $x=0.6$. In agreement with the literature,¹² measurements of T_C as a function of doping (not shown) reveal that T_C falls off rapidly as Co doping increases, which, ignoring effects upon T_C other than those from $N(E_F)$, would suggest that the calculated peak in the DOS at E_F is correct.

Fig. 2 shows a comparison of the valence band photoemission spectra ($h\nu=40\text{eV}$) of $\text{YNi}_{2-x}\text{Co}_x\text{B}_2\text{C}$ ($x=0, 0.6$) together with spectra simulated from the band structure data as described above, in which doping has been approximated by an appropriate downward shift of E_F . For the $x=0.6$ sample, T_C was less than 5K, in comparison to the value of 15.8K for the undoped material, which is in agreement with literature reports.¹² As can be seen in Fig. 2, Co doping does not appear to result in a decrease in spectral weight at E_F - if anything the intensity at E_F is slightly larger in the doped case. There is also extra spectral weight situated between the valence band maximum at 1.25eV BE and E_F for the Co-doped sample. Comparison with the simulated spectra indicates that not only is the spectral weight at E_F not reduced for $x=0.6$, there is also no sign of the shift of the Co-doped spectrum to lower BE's as would be expected within a rigid-band doping scenario. This result is all the more surprising in the light of recent low temperature heat capacity measurements of $\text{YNi}_{2-x}\text{Co}_x\text{B}_2\text{C}$, which show γ -values falling from 19.8 to 8.03 mJ/molK² on going from $x=0$ to $x=0.4$.¹³ As to the reasons behind the disagreement between LDA and PES measurements, apart from electron correlation effects, one should also consider the surface sensitivity of photemission. The fact that bulk probes such as the low temperature specific heat agree with band structure calculations, whilst PES data appear to show a different behaviour, could imply that the surface we prepare prior to PES measurements by scraping of polycrystals in UHV is not representative of the bulk. In this light, it is of interest to note that the only angle-resolved PES study of a cleaved single crystal to date has shown band crossings in agreement with LDA predictions.¹⁴ This trend could be similar to that observed in the high- T_C cuprates, where prior to the availability of high quality single crystals of sufficient size, PES data were prone to the effects of surface contamination.¹⁵ To shed more light on this question, at the time of writing this paper we are carrying out measurements of the B1s core level excitation spectra of the Co-doped samples using electron energy-loss spectroscopy (EELS) in transmission, which is not a surface sensitive

technique. In the past, we have shown that the B1s edges from EELS in transmission give almost quantitative agreement with the B2p partial unoccupied density of states.¹¹

In the space remaining, we would like to present some recent XPS

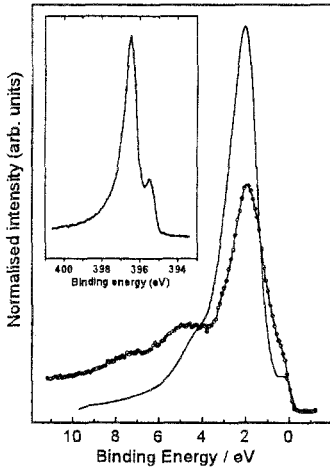


Fig.3. PES spectra of $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ recorded with $\text{AlK}\alpha$ radiation. Main panel: experimental (line and symbols) and calculated (line) valence band spectra, normalised to have equal intensity in their common energy range. The inset shows the N1s core level spectrum.

data from the new superconductor $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_{3-\delta}$ (3223). It is related to the borocarbides in that it possesses a Ni_2B_2 'layer', which in this case is separated by three LaN layers in place of the single RE-C rocksalt layer.⁴ The original hopes that the LaN triple-layer would result in a more pronounced 2-D electronic structure appear to be unfulfilled as the first band structure calculations have been published,^{16,17} showing that the band structure is three-dimensional. Measurements of the superconducting properties of 3223 suggest that it is more suited to the classification as a phonon-mediated BCS superconductor than the $\text{RENi}_2\text{B}_2\text{C}$ materials are.³ Fig. 3 shows the valence band photoemission spectrum of $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ recorded with $\text{AlK}\alpha$ radiation, which favours photoemission from $\text{Ni}3d$ -related bands over that from other states. The

spectrum is very similar to that of $\text{YNi}_2\text{B}_2\text{C}$ (not shown), with the valence band maximum of the boronitride being slightly narrower, and shifted $\sim 0.5\text{eV}$ to higher BE. As can be seen from the figure, the calculated position of the main group of valence bands at BE $\sim 2\text{eV}$ is well reproduced in the experiment, but with the by now familiar discrepancies of a narrower d -valence band and greater spectral weight at higher energies observed in the experiment. The inset shows the N1s core level photoemission spectrum. Two peaks are observed separated by $\sim 0.8\text{eV}$. This is close to the value of 0.75eV predicted for the difference between the BE's of the N atoms situated in the (two) outer and (single) inner LaN layers. The N1s level of the latter should lie at lower BE.¹⁶ However, as is immediately obvious from the figure, the relative intensity of the high BE feature to that at low BE deviates widely from the expected 2:1 intensity ratio, the reason for which is, at present, unclear.

In conclusion, we have presented a comparison between photoemission data from polycrystalline samples of the intermetallic superconductors $\text{YNi}_2\text{B}_2\text{C}$, $\text{YNi}_{2-x}\text{Co}_x\text{B}_2\text{C}$ and $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ and simulated spectra based upon the DOS from LDA band structure calculations. The experiment generally shows no sign of the predicted peak at the Fermi level, and also exhibits a greater spectral weight at higher BE's than predicted. For $\text{YNi}_{2-x}\text{Co}_x\text{B}_2\text{C}$, the PES data are inconsistent with a rigid-band-like behaviour upon Co-doping, the potential reasons for which (electron correlation, surface sensitivity of PES) were briefly discussed. Data from $\text{La}_3\text{Ni}_2\text{B}_2\text{N}_3$ confirm the similarities between the boronitride superconductor with its borocarbide cousins, and the two-peaked N1s XPS spectrum confirms the presence of two inequivalent N sites in the boronitride.

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