Proceedings of the XIII National School of Superconductivity, Lądek Zdrój 2007

XPS Investigation of $Y_{1-x}Dy_xNi_2B_2C$ Superconductors

A. Winiarski, A. Winiarska and Z. Drzazga

August Chełkowski Institute of Physics
Uniwersytecka 4, 40-007 Katowice, Poland

The analysis of the valence band photoemission spectra of $Y_{1-x}Dy_xNi_2B_2C$ ($0 \leq x \leq 1$) is presented. The valence bands are mainly plotted for Ni $3d$, Y $4d$ and Dy $4f$ contributions, according to theoretical predictions. The valence bands of $Y_{1-x}Dy_xNi_2B_2C$ compounds markedly change shape with the x parameter, especially in the binding energy region from 3 eV to 14 eV. For large content of Dy (above 55%) the valence band is predominant by Dy $4f$ states whereas Ni $3d$ states govern the valence band of yttrium rich compounds. Changing in domination of valence sub-band correlates with plot of superconducting transition temperature T_c with Dy concentration.

PACS numbers: 71.20.–b, 74.25.Jb, 74.70.–b, 82.80.Pv

1. Introduction

The interplay of magnetic order and superconductivity makes RNi_2B_2C compounds very interesting for experimental as well as theoretical investigation [1–7]. Earlier we have reported studies on structure and coexistence of superconductivity and magnetism in $Y_{1-x}Dy_xNi_2B_2C$ single crystals [8–10]. The $Y_{1-x}Dy_xNi_2B_2C$ compounds crystallize in tetragonal body-centered $LuNi_2B_2C$-type structure and the lattice parameters in $Y_{1-x}Dy_xNi_2B_2C$ system obey the Vegard law [9]. It follows that superconductivity is strongly influenced by the magnetic subsystem in these compounds. Magnetic ordering in these compounds arises from the rare-earth ions and their $4f$ electrons are responsible for the magnetism. No ordered magnetic moment was detected for Ni.

Following the experimental reports of superconductivity and magnetism in quaternary boro-carbides increasing attention has been paid to the electronic structure calculation of these compounds.

Calculations of the YNi_2B_2C band structure were done using different theoretical methods such as the linearized augmented plane wave (LAPW) method [11], linearized muffin-tin orbital band (LMTO) method [7] or full potential LAPW method [12]. Recently, the band structure of magnetic superconductor $DyNi_2B_2C$ was reported [6].

Relatively few papers are due to investigation of electronic structure by photoemission [4, 13, 14]. In this work special interest is given to the valence band of $Y_{1-x}Dy_xNi_2B_2C$ superconductors investigated by X-ray photoelectron spectroscopy (XPS).

2. Experiment

Polycrystalline samples were prepared by electric arc melting of high purity elements in argon atmosphere. The details of preparation were described in [9]. Temperature of superconducting transition T_c was estimated from dc magnetic susceptibility measurements [9, 10].

X-ray diffraction spectra performed on D5000 X-ray Powder Diffractometer from Siemens confirmed single-phase samples. The samples were broken or scraped with a diamond file under ultra high vacuum conditions for XPS measurements. XPS spectra were obtained at room temperature using a Multitechnique Electron Spectrometer PHI 5700/660 with a monochromatized Al K_α radiation of 1486.6 eV. The energy resolution for XPS is 0.35 eV. The spectra of the valence band were analyzed in detail using Multipak software.

3. Results and discussion

Figures 1 and 2 show the XPS valence bands for chosen compounds of the investigated $Y_{1-x}Dy_xNi_2B_2C$ series. Intensity of peaks was normalized to intensity of the peak at 1.4 eV occurring in all studied compounds. It follows from Fig. 1 that valence band spectrum of YNi_2B_2C is markedly different from $DyNi_2B_2C$ one. The peak at binding energy about 1.4 eV with a shoulder at about $E_b = 2.4$ eV is connected predominantly with nickel density of state and it is seen for both compounds. However, this broad peak comes from Ni $3d$ states, which can be hybridized with $2p$ states of B and C atoms as shown by theoretical calculations by Lee et al. [7]. Spectrum of $DyNi_2B_2C$ magnetic superconductor reveals additionally two high peaks at binding energy of 4.6 eV and 9.0 eV, which correspond to Dy $6s$ and Dy $4f$ states.

The valence band spectra of mixed $Y_{1-x}Dy_xNi_2B_2C$ compounds are presented in Fig. 2. Dysprosium substitution instead yttrium atoms changes systematically the valence band in the binding energy region from 3 eV to 14 eV. The valence band spectra show four to five features located approximately at the binding energies 1.4 eV, 4.6 eV, 8.3 eV, 9.7 eV and 12.6 eV. The binding energy of the features does not depend on the dysprosium content. It is important to see that for Dy content larger than $\approx 55\%$ the valence band is dominated by Dy $4f$ states whereas Ni $3d$ states govern the valence band for yttrium rich compounds.

It should be noted that comparison of changes in the intensity of Dy $4f$ peaks (Figs. 1 and 2) and superconducting transition temperature T_c (Fig. 3) as a function of dysprosium concentration points out to nearly constant T_c for Dy-rich superconductors and markedly increasing T_c for Y-rich compounds.

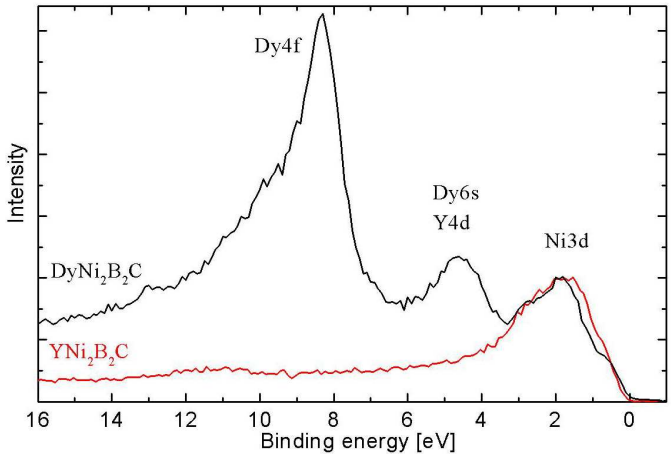

Fig. 1. The valence band spectra of $DyNi_2B_2C$ and YNi_2B_2C. The spectra are normalized to the Ni $3d$ feature.

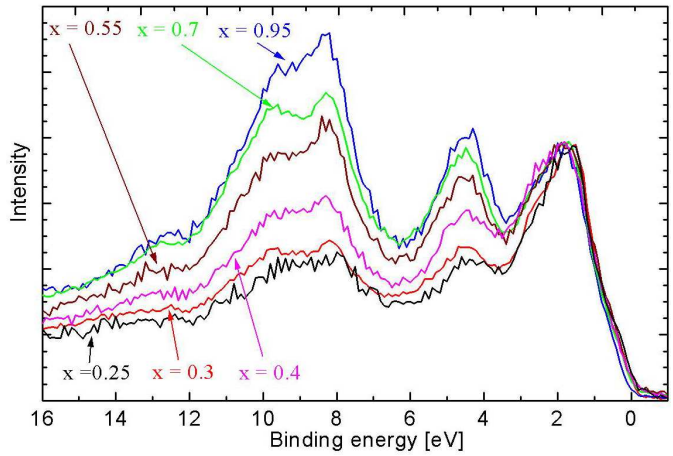

Fig. 2. The valence band spectra of $Y_{1-x}Dy_xNi_2B_2C$ series.

It is interesting to note that Dy $4f_{7/2}$ and Dy $4f_{5/2}$ states are seen separately in mixed compounds unlike pure $DyNi_2B_2C$. The features at 8.3 eV and 9.7 eV consist mainly of Dy $4f$ states with a small contribution of Y $4d$, Ni $3d$, Ni $5s$, B $2p$, and C $2p$ bands. Feature at 4.3 eV comes mainly from Dy $6s$ states with a small contribution of Y $4d$. For very Dy-rich compounds ($x > 0.9$) this peak is higher than the peak with binding energy about 1.4 eV (Ni $3d$ state). The feature at 12.6 eV corresponds to Dy $4f$, however small contributions of Y $4d$, B $2s$ and C $2s$ bands are possible. It should be noticed that a little shift of the Ni $3d$ band towards higher binding energy is observed in rich Dy compounds in comparison with nonmagnetic superconductor YNi_2B_2C (Figs. 1 and 2).

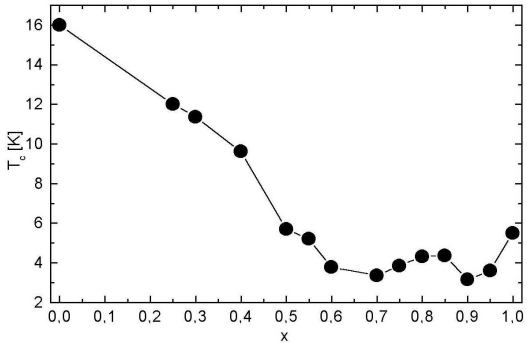

Fig. 3. Superconducting transition temperature T_c as a function of dysprosium content.

4. Conclusions

The valence bands of $Y_{1-x}Dy_xNi_2B_2C$ compounds markedly change shape with the x parameter, especially in the binding energy region from 3 eV to 14 eV. Dy $4f$ states are predominant for Dy content larger than 55%. Domination of Dy $4f$ states in the valence band correlates with nearly stabilized superconducting transition temperature T_c for Dy-rich compounds.

References

[1] M.D. Lan, T.J. Chang, C.S. Liaw, *J. Phys. Chem. Solids* **59**, 1285 (1998).

[2] P. Allenspach, U. Gasser, *J. Alloys Comp.* **311**, 1 (2000).

[3] J. Freudenberger, G. Fuchs, K. Nenkov, S.-L. Drechsler, K.-H. Mühler, L. Schultz, *Physica C, Superconductivity* **339**, 195 (2000).

[4] S.M. Loureiro, C. Kealhofer, C. Felser, R.J. Cava, *Solid State Commun.* **119**, 675 (2001).

[5] K.-H. Müller, V.N. Narozhnyi, *Rep. Prog. Phys.* **64**, 943 (2001).

[6] A.O. Shorikov, V.I. Anisimov, M. Sigrist, *J. Phys., Condens. Matter* **18**, 5973 (2006).

[7] J.I. Lee, T.S. Zhao, I.G. Kim, B.I. Min, S.J. Youn, *Phys. Rev. B* **50**, 4030 (1994).

[8] Z. Drzazga, A. Winiarska, A. Winiarski, D. Kaczorowski, *Acta Phys. Pol. A* **97**, 221 (2000).

[9] Z. Drzazga, D. Kaczorowski, A. Winiarska, A. Winiarski, *J. Alloys Comp.* **323-324**, 562 (2001).

[10] Z. Drzazga, A. Winiarska, D. Kaczorowski, *J. Magn. Magn. Mater.* **242-245**, 829 (2002).

[11] L.F. Mattheiss, *High-T_c Update* **8**, 2 (1994).

[12] K. Yamauchi, H. Katayama-Yoshida, A. Yanase, H. Harima, *Physica C* **412-414**, 225 (2004).

[13] J. Wang, X. Zhang, Y. Ruan, Z. Jiao, Q. Zhang, Ch. Fan, X. Zhang, Y. Su, G. Cao, *Physica C* **282-287**, 1935 (1997).

[14] L.-S. Hsu, C.-J. Chen, M.-D. Lan, *J. Alloys Comp.* **397**, 23 (2005).