Electronic Structure and Superconductivity of Nonmagnetic Transition Metal Borocarbides

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The electronic structure of tetragonal $(\mathrm{RC(N)})_\mathrm{m}(\mathrm{TB})_2$, *m=1-3, compounds, with* R= Y,Lu,La, T=Ni,Pt *is studied. Total and partial densities of states* $N(E)$ *are calculated and compared with orbital resolved x-ray absorption data. Special attention is paid to the structure of* $N(E)$ *near the Fermi-level and its consequences for thermodynamic properties in the superconducting and the normal states. A medium el-ph coupling constant* $0.5 \leq \lambda \leq 1.2$ *is found. There is no simple correlation between* $N(0)$ *and* T_c. *The analysis of the upper critical field reveals the presence of at least two groups of electrons with quite different Fermi velocities* v_F *in accord with dHvA data, and with calculated distributions of* v_F *around the Fermi surface. PACS numbers: 05.70 Ln, 05.70 Jk, 64.*

1. INTRODUCTION

Five years after the discovery of rare earth transition metal borocarbides (nitrides) RTBC(N) with T=Ni,Pd,Pt transition metals, the place of RTBC(N) compounds within the family of novel superconductors is still under debate. In contrast to first speculations of a similarity to quasi-2D cuprates (suggested by their reminiscent transition metal layered crystal structure), various LDA (local density approximation) band structure calculations performed in 1994/95 clearly demonstrated their 3D electronic structure.[1] Consequently, the whole class has been classified as traditional superconductors, closely related to the A-15's or to other intermetallic compounds. Finally, in the context of anisotropy and other unusual properties, *d*-wave superconductivity has been proposed for YNi_2B_2C and $LuNi_2B_2C$.[3,12] Thus the question arises whether RC(N)TB are 3D counterparts of the 2D-cuprates? A detailed knowledge of the electronic structure is probably the most important starting point to understand the superconducting pecularities of these compounds using susequently a more microscopic approach.

2. ELECTRONIC STRUCTURE

All bandstructure calculations for RC(N)TB compounds, including ours, reveal sizeable dispersion in the c-direction of three to five narrow bands crossing the Fermi energy E_F. Electronically the coupling of the 2D-$(TB)_2$ networks is mediated mainly by the C/N $2p_z$ states which strongly hybridize with B $2p_z$ states. Despite this coupling which ensures the 3D-character of the electronic structure and only moderate anisotropies of normal and superconducting properties, the whole RC-layer derived states act as a charge rerservoir for the $(TB)_2$ networks (like the so called blocklayers in the cuprates). Then under certain circumstancs a flat band with predominant T derived d states gives rise to narrow asymmetric peaks in the total and partial densities of states $N(0)$ (DOS) near E_F. To our knowledge the origin of this peak has not yet been completely clarified. Is it the remnant of a van Hove singularity which might occur at some special B-T-B bond angle? Comparing the electronic structure of various RCTB-compounds one observes an increase of the maximum of $N(E)$ with increasing B-T-B bond angle and splitting of this peak in some special cases due to relativistic effects for compounds with $5d$ electrons near E_F (T=Pt) and or large R ions (e.g. $LaC(NiB)_2$ and $LaC(PtB)_2$[4]). Within this picture the DOS remains relatively flat at an energy range of $\sim T_c$ and at a low-frequency phonon scale. Then the total electron-phonon coupling constant λ_{el-ph} can be estimated from the comparison of $N(0)$ with the experimental value of the Sommerfeld constant γ_n. As a result we arrive at a medium coupling strength λ_{el-ph} from 0.5 to 1.2 for 7 compounds where γ_n data are available (see Fig. 2 of Ref. 4). In contrast with this relalively uniform behaviour no simple correlation between the calculated $N(0)$ value and the observed critical temperature T_c has been found for the 10 compounds considered. Especially the absence of superconductivity or low T_c value for $LaC(NiB)_2$ and $LaC(PdB)_2$, respectively, compared with superconducting $LaC(PtB)_2$ ($T_c \approx 12$ K) with a significantly lower $N(0)$ value is noteworthy. However such an analysis should be taken with some caution, if $N(E)$ near E_F must be described by a real singularity, since then all thermodynamic characteristics are affected by the former. As a consequence the estimated above λ_{el-ph} values should be regarded as an upper bound.

Experimentally the existence of peaks near E_F has been confirmed by polarization-dependent XAS (X-ray absorption spectroscopy) measurements for C $1s \rightarrow 2p_z$ and B $1s \rightarrow 2p_z$ transitions.[4,5] However, the covalency of the short C-B bond seems to be somewhat overestimated by the LDA predicting a smaller out of plane anisotropy than it is reflected in the XAS data(see Fig. 1, left panel).

3. SUPERCONDUCTING PROPERTIES RELATED DIRECTLY TO THE ELECTRONIC STRUCTURE

The most impressive connection between the electronic structure and superconducting properties comes from the upper critical field $H_{c2}(T)$. Analyzing the absolute value of $H_{c2}(0)$ in terms of the traditional effective isotropic single band (ISB) approach using the averaged Fermi velocities v_F derived from the LDA band structure calculations, one arrives at much too small values of the order of 2 to 3 T to be compared with the experimental values of about 8 to 11 T for clean samples

(see Fig. 1, middle panel). In addition the unusual positive curvature near T_c is not reproduced. However, assuming the existence of at least two groups (bands) of electrons with significantly different Fermi velocities $v_{F2}/v_{F1} \sim 5$, both problems could resolved.[6] Thereby small impurity scattering rates γ_{imp} derived from de Haas van Alphen (dHvA) measurements are taken into account.

Nearly the same ratio (up to 6) was found a posteriori in our analysis of the v_F-distribution over the Fermi surface for $LuC(NiB)_2$. Quite interestingly, we found also that the slow electrons stem from parts of the Fermi surface exhibiting nesting properties. Closely related wave vectors seem to occur also in low-frequency phonons exhibiting anomalous softening from 7 mev to 4 meV entering the superconducting state[7] as well in the so called incommensurate a-axis modulated magnetic structure.[8]

4. MODERATE SUPPRESSION OF SUPERCONDUCTIVITY IN PSEUDOQUATERNARY COMPOUNDS

The controlled substitutional disorder at the R(T) site such as in $Y_xLu_{1-x}C(NiB)_2$[9] or in $YC(Ni_{1-x}Pt_xB)_2$[2] allows new insight in the specific role of the two borocarbide subsystems: the $(TB)_2$-networks and the charge reservoir RC(N) layers. In addition, for high-quality, pure systems the transition from clean to dirty limit superconductors can be investigated in detail. In general, nonlinear x-dependences have been observed for almost all physical quantities.[9] Near the clean limit the upper critical field is the most sensitive quantity affected negatively by weak disorder. In particular, the value of $H_{c2}(T)$ at T=0 and its positive curvature near T_c measure the sample quality or purity, i. e. in our case the x-dependence. All available experimental data can be described in wide temperature intervals $\sim 0.3T_c \leq T \leq 0.95T_c$ using only two effective parameters $H^*_{c2}(x) > H_{c2}(0)$ and $\alpha \geq 0$ by the simple scaling law:

$$H_{c2}(T,x) = H^*_{c2}(x)(1 - T/T_c(x))^{1+\alpha(x)}, \tag{1}$$

where their substitutional disorder dependence can be described typically by one or few additional small parameter(s) $0 \leq f_A \ll 1$

$$A(x) = (xA_{R'} + (1-x)A_{R''})\,(1 - f_A \sin(0.5\pi x)), \tag{2}$$

or combinations of that (for examples , see below), where A_R stands for any quantity A in the pure R(T) system. We note that for the linear specific heat γ_s in the vortex state $H_{c1}<H<H_{c2}$ similar disorder dependent scaling laws have been observed[2]

$$\gamma_s = \gamma_n T\,(H/H_{c2})^{1-\beta(x)}\,, \tag{3}$$

where the exponent β tends to 0(0.5) in the dirty(clean) limit, similarly as the curvature exponent α introduced in Eq. (1). Wether $\alpha \approx \beta$ holds or not also in the intermediate x-region should be elucidated in future. Since at present the available data doesn't allow any definite conclusion. Analogously the RCTB-value (saturation) for α in the absolutely clean limit case is not yet known. (At present our best borocarbide single crystals with residual resitivity ratios exceeding 40, show

$\alpha \approx 0.43$ derived from resistivity measurements) In the clean limit of $NbSe_2$ (s-wave superconductor) one arrives at $\beta \approx 1/3$[2,13] whereas in clean d-wave superconductors 0.5 to 0.59 have been predicted theoretically.[10] If one substitutes in the weakly coupled charge reservoir subsystem isoelectronic R' ions for R with similar ionic radii, modest disorder effects are expected in contrast to substitutions in the TB-network, e. g. in $YC(Ni_{1-x}Pt_xB)_2$, where already for $x = 0.2$ the dirty limit $\alpha = 0$ has been reached. In the $Y_xLu_{1-x}C(NiB)_2$ system a minimum of $\alpha \approx 0.1$ to 0.16 occurs near x=0.5 to 0.6. In the same fashion $H_{c2}(x,T)$ for $YC(Ni_{1-x}Co_xB)_2$[11] can be explained, where due to the enhanced scattering rate related to the non-isoelectronic substitution in the TB-network the dirty limit is reached very fast: $\alpha(x \approx 0.06) \approx 0$. According to ouri calculations performed within the coherent potential approximation (CPA) for $LuC(Ni_{1-x}Co_xB)_2$ the scattering strength of Co is about 20 times stronger compared with the Y-Lu case considered below. Within the multiband Eliashberg theory the transition from the clean to the dirty limit can be described quantitatively in terms of the vanishing field curvature exponent α, if the considered disorder under consideration acts mainly as interband scattering.

Quite remarkably, a linear correlation between T_c and $\gamma_n \propto N(0)(1+\lambda)$ has been observed by Michor *et al.*[14] for $Y_xLu_{1-x}C(NiB)_2$. Combining our CPA-calculation results for the total density of states $N(0)$ with this finding and Eq. (2), we write

$$\begin{aligned} T_c &= a + b\,(xN_Y + (1-x)N_{Lu})\,(1 - f_N \sin(0.5\pi x)) \times \\ &\quad [1 + (x\lambda_Y + (1-x)\lambda_{Lu})\,(1 - f_\lambda \sin(0.5\pi x))]\,, \end{aligned} \tag{4}$$

where b=2.08 $10^7 K^2$ and N_Y=4 states/(eV unit cell) and $N_{Lu} = 4.2$ obtained for the pure systems and λ_Y=1.05 as well as λ_{Lu}=1.09 (derived from the experimental γ_n values) have been used. The CPA calculations reveal a very smooth $N(x)$-dependence which can be approximated by f_N=0.015 and Eq. (2). Since local relaxations have been ignored so far, we adopt a twice as large value of f_N=0.03 in estimating the total disorder effect. So we arrive at a much larger value f_λ=0.09 (see Fig. 1 right panel). Our results suggest that the suppression of superconductivity is governed mainly by the disorder induced weakening of the electron-phonon coupling constant λ. Taking into account the DOS dependence of $\lambda = N(0)\langle V\rangle_{FS}$ we would arrive at a somewhat smaller but nevertheless predominant change of the electron-phonon interaction $\langle V\rangle_{FS}$ (averaged over the Fermi surface) $f_V \approx 0.06$. Alternatively, assuming no disorder effect upon λ, a very strong $N(0,x)$ dependence would follow: f_N=0.09 (see the broken line in Fig. 1c).

5. CONCLUSION

Several details of the superconducting state of RC(N)TB compounds are not yet fully understood. But despite some subtle points, at the present time there is a reasonably qualitative agreement between the predictions of the LDA calculations for the electronic structure and the available experimental data. For this reason we believe that the predictions of a full anisotropic, (multiband) version of the Eliashberg theory taking into account also the possibly peculiar structure of $N(E)$ should be awaited before exotic pairing mechanisms must be considered in detail.

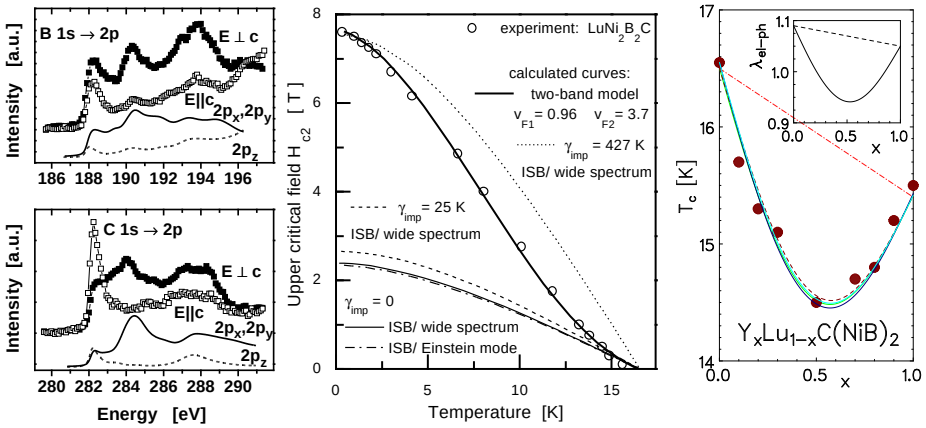

Fig. 1. **left.)**Polarization-dependent XAS spectra of single crystal $YC(NiB)_2$ with the electric field $\parallel$ and $\perp$ to the c-axis. The corresponding m-resolved partial DOS from our LDA calculations are denoted by dashed and full lines (broadened to account for life-time and finite resolution). **middle.)** Experimental data for H_{c_2} of $LuC(NiB)_2$ (magnetic field $\parallel$ c-axis) compared with theoretical curves: (i) the isotropic single band (ISB) model with $v_F = 2.76 \times 10^7$ cm/s and various impurity scattering rates γ_{imp}; (ii) the two-band model with v_{Fi} (i=1,2) in units of 10^7 cm/s. **right.)** Critical temperature T_c *vs.* concentration in the $Y_xLu_{1-x}C(NiB)_2$ using experimental data [9,11] In the inset the phenomenological concentration dependence of the total electron-phonon coupling constant λ_{el-ph} derived from our CPA analysis for $N(0)$ and Eq. (4) is shown.

ACKNOWLEDGMENTS

This research is supported by the Deutsche Forschungsgemeinschaft and the SFB 463. Further thanks to H. Michor and A. Kreyssig for providing us with the experimental data prior to publication and for discussions.

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