Structural properties of $Y_{1-x}Yb_xNi_2B_2C$ synthesized at high pressure: EXAFS data analysis

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Local structure of $Y_{1-x}Yb_xNi_2B_2C$ series synthesized at high pressure 8 GPa has been studied using EXAFS. Measurements were performed at the Ni K-edge in temperature range 5-300 K. The results show that the Debye-Waller factor for Ni-Ni bond in the parent YNi_2B_2C compound is characterized by the Einstein temperature $\Theta_E = 350$ K, while a minimum value $\Theta_E = 300$K is reached for the compound with $x = 0.025$, which has the highest critical temperature $T_c = 12.5$K of the superconductive transition. This correlates with the further suppressing of superconductivity and with the appearance of the local magnetic moments in the investigated $Y_{1-x}Yb_xNi_2B_2C$ series for $x \geq 0.05$ compounds. Observed changes in the local electronic and the local crystal structure of this system as a function of Yb concentration and of temperature were explained in the frame of the band filling effect.
Keywords: EXAFS; **local structure**; **high pressure.**

1. Introduction

The recent discovery (Cava *et al.*, 1994; Nagarajan *et al.*, 1994) of superconductivity with transition temperatures up to 16.6 K in the quaternary intermetallic RNi_2B_2C materials (R is a rare earth ion) has attracted a great deal of attention because of their interesting superconducting and magnetic properties and of interaction between them. This class of materials exhibits a variety of phenomena such as fairly high superconducting transition temperature in RNi_2B_2C (R=Sc,Y,Lu) (Ku *et al.*, 1994), coexistence of superconductivity and magnetism in RNi_2B_2C (R=Ho,Er,Tm,Dy) (Tomy *et al.*, 1995; Cho *et al.*, 1995), heavy fermion behavior in $YbNi_2B_2C$ (Yatskar *et al.*, 1996). The crystal structure of the family of rare-earth nickel borocarbide (RNi_2B_2C) is a carbon-filled variant of the $ThCr_2Si_2$-type tetragonal body-centered (space group $I4/mmm$) structure.

In spite of the fact that there are a lot of investigations made with these compounds, it is desirable to get a better understanding of the interplay between the changes in the electronic and local structure properties depending on temperature, concentration of doped atoms and pressure. EXAFS (Extended X-ray Absorption Fine Structure) is a very useful technique for probing the local structure of the compound, which allows one to observe the unique peculiarities of the lattice dynamics and of valence states of the absorbing atoms. It is the purpose of this paper to study the influence of Yb- doping on the local structure of YNi_2B_2C and to connect the local structural changes with changes in the macroscopic properties from the superconducting state at the Y-end of the $Y_{1-x}Yb_xNi_2B_2C$ series to the heavy-fermion behavior at the Yb-end.

2. Experimental and data analysis

Since it is impossible to synthesize Y-Yb compounds at normal conditions, the samples $Y_{1-x}Yb_xNi_2B_2C$ with $x = 0.0; 0.01; 0.025; 0.05; 0.10; 0.15; 0.4; 1.0$ were prepared at high pressure up to 8 GPa by melting YNi_2, $YbNi_2$, boron and carbon in the chamber of the "Toroid" type cell (Khvostantsev *et al.*, 1977). The preparation procedure is described by Tsvyashchenko (1984). Compounds with $x < 0.05$ demonstrate superconductivity with $T_c = 8.2$ K, 10.5 K and 12.5 K for $x = 0$, 0.01 and 0.025, respectively. Down to T= 4.21 K no superconductivity was found for compositions with $x \geq 0.05$. At the same time the magnetic susceptibility slightly decrease with temperature decreasing at $T>T_c$ for superconductive compounds. It is practically independent of temperature for $x = 0.05$, increases with temperature decrease for $x \geq 0.05$ and follows to Curie-Weiss law for $YbNi_2B_2C$. From such a behavior we conclude that the local magnetic moments occur for $x \geq 0.05$ and tend to be ordered at higher Yb content. All the samples were pure phase ones, as examined by X-ray diffraction. Since the high pressure synthesize produces the metastable phases of the compounds (Tsvyashchenko *et al.*, 1997), several samples of YNi_2B_2C were annealed in high vacuum at 500° C during 4 hours to compare the local structure of YNi_2B_2C synthesized at high (8 GPa) and at normal pressure. This procedure practically restores the critical temperature value $T_c \approx 15.6$ K typical for the normal pressure synthesis. So we note in this text such samples as 'synthesized at normal pressure' or 'normal pressure samples'.

The X-ray absorption measurements above K-Ni edge were carried out on D21 beam line of DCI storage ring (LURE, Orsay, France), using Si [311] double-crystal monochromator, and on the D2 beam line of DORIS III storage ring (DESY, Hamburg, Germany), using Si(111) double-crystal monochromator. The storage rings were operated with a positron beam energy 1.85 GeV and 4.6 GeV and maximum current 300 mA and 150 mA for DCI and DORIS III respectively. The energy resolution was estimated as 2 eV at 8 keV.

In general, the EXAFS signal is a sum of paths including both single-scattering (SS) and multiple-scattering (MS) contributions (Stern & Heald, 1983): $\chi(k) = \sum_\Gamma \chi_\Gamma(k)$. The contribution of each path can be expressed in the form:

$$\chi(k) = \frac{NS_0^2}{kr^2} F(k) \sin[2kr + \phi(k)] e^{-2k^2\sigma^2} e^{-2r/\lambda(k)} \qquad (1)$$

where k is the photoelectron wave number, S_0^2 is the passive electron reduction factor accounting for shake-up and shake-off processes, N is a coordination number of the shells of neighboring atoms in the case of the SS path or the number of equivalent scattering configurations in the case of the MS paths, r is half of the total scattering path length, σ^2 is the corresponding mean-square relative displacement (Debye-Waller factor), $F(k)$ and $\phi(k)$ are the effective scattering amplitude and phase shift respectively, and $\lambda(k)$ is the mean free path. $F(k)$, $\phi(k)$ and $\lambda(k)$ were calculated for the reference same body-centered tetragonal ($I4/mmm$) structure of YNi_2B_2C using the FEFF6 code (Zabinsky *et al.*, 1995). The data have been analysed using the computer program packages EXPROG (Notling & Hermes, 1992), EXCURVE (Binsted *et al.*, 1992) and VIPER (Klementev, 2000).

3. Results and discussion

It was found that the length of Ni-Ni bond slightly increases with temperature and is varied from 2.48 Å to 2.49 Å, which is shorter than in metallic nickel (2.51 Å), suggesting strong metal-metal bonding. The length of Ni-B bond becomes to increase when the concentration of Yb exceeds $x = 0.1$ and is varied from 2.14 Å (for $x = 0$) to 2.18 Å (for $x = 1.0$). The Debye-Waller factors for Ni-B bond have rather high values implying a soft behavior for this bond. They increase with temperature and reach maximum values for the first and last samples in the $Y_{1-x}Yb_xNi_2B_2C$ series with Yb concentration $x = 0.0$ and $x = 1.0$, respectively. The Debye-Waller factors for Ni-Ni bond also increase with temperature, they are characterized by the Einstein temperature 350 K, but within the Yb concentration range, a minimum value is reached at $x = 0.025$ (Einstein temperature 300 K) (see Fig. 1). It correlates with the further suppressing of superconductivity and with the appearance of the local magnetic moments in the investigated $Y_{1-x}Yb_xNi_2B_2C$ series.

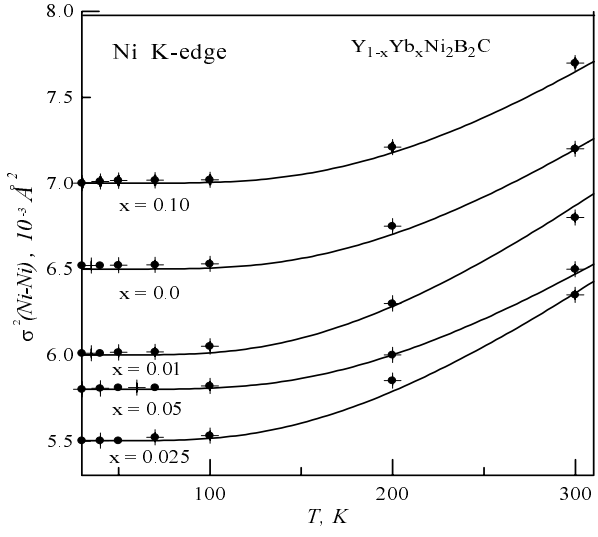

Figure 1
Temperature dependence of Debye-Waller factor for Ni-Ni bond in the $Y_{1-x}Yb_xNi_2B_2C$ ($x = 0.0; 0.01; 0.025; 0.05; 0.10$) series in the range 30-300K. Einstein model curves are shown as solid lines. Einstein temperatures Θ_E equal to 350K, 310K, 300K, 340K, 370K for $x = 0.0; 0.01; 0.025; 0.05; 0.10$ respectively.

The Fourier transformed spectra of $Y_{1-x}Yb_xNi_2B_2C$ samples (see Fig. 2) contain a peak at 4.5-5.0 Å, which cannot be explained within single-scattering theory (dashed curve). Taking into account double and triple scattering processes (paths DS and TS in the inset of Fig. 2) allows us to fit this peak with good accuracy. Thus, there is a short-range order in the Ni-Ni sub-lattice in the direction [010] and [100] which leads to the strong "focusing" effect in the EXAFS spectra. The absence of a peak in the range of 3.5-4.0 Å indicates that there is a substantial disorder in the Ni-Ni sub-lattice within [110] directions.

The results obtained from EXAFS measurements at Ni K-edge in the $Y_{1-x}Yb_xNi_2B_2C$ series reveal the close relationship between the changes in the electronic and magnetic properties and in local structure, against temperature and Yb content. As it was shown earlier (Tsvyashchenko & Fomicheva, 1989), the valency of the ytterbium transition metal in $Y_{1-x}Yb_x$ binary alloys strongly depends on the Yb concentration. It allows us to consider the changes in the properties of $Y_{1-x}Yb_xNi_2B_2C$ in terms of the valence of ytterbium atoms.

At small Yb content (up to $x = 0.025$), doped Yb ions have the lowest valence Yb^{2+}. Therefore the hybridization between Y(Yb)-Ni bonds becomes lower with doping and the electronic filling of Ni 3d band slightly increases. This leads to the softening of the phonon modes and the decrease of the Einstein temperature (from 350 K for YNi_2B_2C - high pressure phase to 300 K for the compound with $x = 0.025$). Thus, the increase of the Ni density of states at Fermi level $N(E_F)$ and the decrease of the averaged phonon frequency promote the T_c increasing from 8.2 K for the parent compound YNi_2B_2C to 12.5 K for $Y_{0.975}Yb_{0.025}Ni_2B_2C$ sample (both samples were prepared at high pressure 8 Gpa). The further substitution of Y atoms by Yb atoms causes the transformation of Yb^{2+} ions to Yb^{3+} (Tsvyashchenko & Fomicheva, 1989). This results in the opposite effect: the electronic filling of 3d Ni band decreases as well as the Ni contribution to the density of states at the Fermi level $N(E_F)$ decreases. A similar scenario was observed in the $YNi_{2-x}Co(Cu)_xB_2C$ series (Ravindran *et al.*, 1998) by substituting Ni by Co(Cu). The Einstein temperature grows from 300 K for $Y_{0.975}Yb_{0.025}Ni_2B_2C$ to 370 K for $Y_{0.90}Yb_{0.10}Ni_2B_2C$ which effectively reduces the electron-phonon coupling constant. Hence, the superconductivity in $Y_{1-x}Yb_xNi_2B_2C$ (for $x > 0.025$) is suppressed. Another reason for superconductivity breaking is the above mentioned appearance of the local magnetic moments in compounds with $x \geq 0.05$. It is worthwhile to notice that $Y_{0.975}Yb_{0.025}Ni_2B_2C$ sample with the highest T_c has the minimum static Debye-Waller factor, which points to the lowest disoder in the Ni-Ni sub-lattice at this Yb doping level.

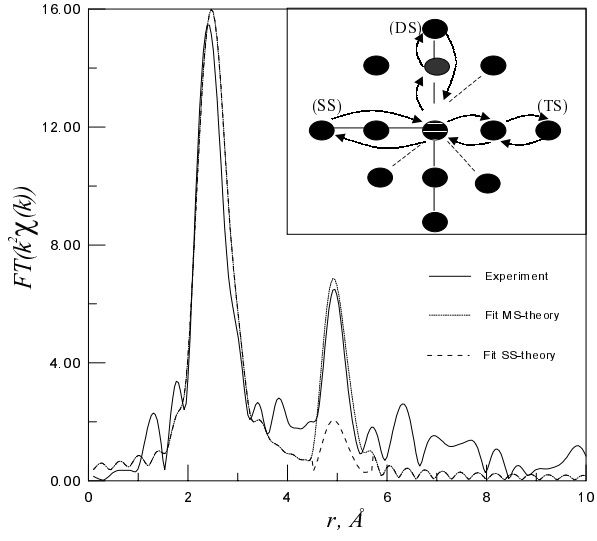

Figure 2
Fourier transformed data (solid curve) and the fits with single-scattering (SS) theory (dashed curve) and multiple-scattering (MS) theory (dotted curve) for YNi_2B_2C at 30K. Inset: possible paths for scattering in the Ni-Ni sub-lattice in the $Y_{1-x}Yb_xNi_2B_2C$: SS - single scattering path, DS - double scattering and TS - triple scattering path.

So, our findings point out the close interrelation between the local structure of $Y_{1-x}Yb_xNi_2B_2C$ and its superconducting and magnetic properties. However, the reasons for the strong sensitivity of the superconducting range to very small changes in Yb content from $x = 0.025$ to $x = 0.05$ should be additionally studied.

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