The effect of hydrogenation upon superconductivity in layered La$_3$Ni$_2$B$_2$N$_{3-\delta}$

M. Sieberer$^a$, H. Michor$^{a,*}$, S. Manalo$^a$, M. Della Mea$^a$, G. Hilscher$^a$, A. Grytsiv$^b$, P. Rogl$^b$

$^a$Institut für Festkörperphysik, T.U. Wien, A-1040 Wien, Austria
$^b$Institut für Physikalische Chemie, Universität Wien, A-1090 Wien, Austria

Abstract

We report on hydrogenation of the layered boronitride superconductor La$_3$Ni$_2$B$_2$N$_{3-\delta}$. Bulk specimen have been hydrogenated at 27 bar and temperatures ranging from 70 to 120°C yielding a series La$_3$Ni$_2$B$_2$N$_{3-\delta}$H$_x$ with $x = 0.6$ and 1.0 which exhibits a rather small volume expansion, $\Delta V/V \approx 0.05\%$ f.u. hydrogen. Specific heat and magnetic susceptibility studies of samples with $x = 0$, 0.6, and 1.0 reveal a clear bulk effect of hydrogenation upon the superconducting properties, e.g., an increase of $T_c$ by about 0.5 K, as well as an increase of $H_c(T)$ and $H_{c2}(T)$.

© 2006 Elsevier B.V. All rights reserved.

PACS: 74.70.Dd; 74.62.Dh; 74.25.Bt

Keywords: Boronitrides; Superconductivity; Hydrogen

La$_3$Ni$_2$B$_2$N$_{3-\delta}$ is superconducting below 12 K and belongs to the family of lanthanum nickel boronitrides (LaNi)$_n$Ni$_2$B$_2$ with $n=2,3$ which are closely related to the RNi$_2$B$_2$C superconductors. Its structure is body-centered tetragonal with rocksalt-type LaNi triple-layers in between NiB layers, thus, forming a natural ABAB...heterostructure [1]. La$_3$Ni$_2$B$_2$N$_{3-\delta}$ has been characterized as an anisotropic $\delta$-wave superconductor with dual band characteristics [2-4]. In the present paper we studied the effect of hydrogenation. Earlier studies on the related borocarbide YNi$_2$B$_2$C have not revealed any significant hydrogen absorption [5].

Large polycrystalline pieces of La$_3$Ni$_2$B$_2$N$_{3-\delta}$ have been prepared by inductive levitation melting of a La$_3$Ni$_2$B$_2$ precursor alloy in Ar/N$_2$ atmosphere such that the $N$-stoichiometry has been increased slowly to 2.8(1)/f.u. The samples were finally annealed in a vacuum furnace at 1100°C for 1 week. Hydrogenation studies were performed with 1 g solid pieces (all taken from one well characterized 12 g specimen) in a high pressure system with in situ measurement of the mass change using a Sartorius microbalance performing at an accuracy of 10 μg. The final hydrogen content has been determined from the difference between the initial sample mass after heating in vacuum and the final mass after hydrogen charging and holding the samples one week in high vacuum at room temperature.

A series La$_3$Ni$_2$B$_2$N$_{3-\delta}$H$_x$ has been prepared which includes the initial material ($x=0$) and hydrogenated samples with $x \approx 0.6$ and 1.0. The process parameters were hydrogen pressures of 27 bar and maximum temperatures hold for 24 h at 70, 120, and 200°C in three different runs. The 200°C run resulted in a disintegrated and partly decomposed sample, whereas the 70°C and 120°C runs yielded essentially single phase samples with $x \approx 0.6$ and $x \approx 1.0$, respectively, without any obvious disintegration of the sample pieces. The verification of the phase purity and the evaluation of the lattice parameters has been done via powder X-ray diffractionmetry with a Guinier–Huber camera equipped with an image plate revealing just traces of impurity phases. Hydrogenation results in a very small increase of the cell volume from 2.1901(2) nm$^3$ for $x = 0$ to

$^\dagger$ The work was supported by the Austrian Science Foundation Fonds, P-16250-Phy.

$^*$Corresponding author. Tel.: +43 1 58801 13140. fax.: +43 1 58801 136199.

E-mail address: michor@ifp.tuwien.ac.at (H. Michor).
2.191(1) nm$^3$ for $x = 1$, indicating that the H-atoms at least partially occupy voids in the structure, e.g. empty nitrogen sites or interstitial sites.

In order to study the effect of hydrogenation upon the superconducting properties specific heat in magnetic fields up to 9 T and AC susceptibility measurements have been performed. The specific heat data (see Fig. 1) clearly reveal an increase of $T_c$ from 12.6(2) K for $x = 0$ to 13.1(2) K for $x = 1$, i.e. with an approximate rate of $+0.5(3)$ K/f.u.-H.

The variation of the normal state electronic specific heat coefficient $\gamma$ upon hydrogenation is rather insignificant with $\gamma \approx 27(1)$ mJ/molK$^2$ (see Fig. 1). The phonon contribution to the normal state specific heat on the other hand reveals a significant lattice softening, thus, indicating a correlation between the raise of $T_c$ and the decrease of the Debye temperature $\Theta_D \approx 321(4)$ K for La$_3$Ni$_2$B$_2$N$_3$-δ and 304(3) for La$_3$Ni$_2$B$_2$N$_3$H$_{1.0}$. A similar change of $\Theta_D$ (with opposite sign) was also observed by hydrostatic pressure experiments on La$_3$Ni$_2$B$_2$N$_3$-δ when comparing ambient pressure and 1.2 GPa data [2]. The latter, however, relates to an approximately twenty times larger volume change (estimated by assuming a typical bulk modulus of 200 GPa) than that caused by 1 f.u. hydrogen in the lattice. This indicates that the softening of the lattice upon hydrogenation may be caused by changes of the electronic structure.

The analysis of the specific heat data (as done in Ref. [2]) reveals that the raise in $T_c$ is accompanied by an increase of the thermodynamic critical field, $H_c(0)$, from 156 to 167 mT (see Fig. 2). A corresponding increase of the upper critical field $H_{c2}$ is shown in Fig. 3. The analysis of the upper critical field $H_{c2}(T)$ in the scope of a two-band Eliashberg theory [3] clearly reveals two-band effects (positive curvature for $T \approx T_c$) for the untreated sample. Absorption of hydrogen appears to reduce the curvature of $H_{c2}(T)$ near $T_c$ which is tentatively attributed to increased impurity scattering caused by hydrogenation.

Summing up, hydrogenation of La$_3$Ni$_2$B$_2$N$_3$-δ yields an increase of the transition temperature by about $+0.5$ K/f.u.-H, as well as enhanced thermodynamic and upper critical fields. Analyzing this behavior in the scope of the Eliashberg theory indicates that hydrogenation leads to a stronger electron–phonon coupling mainly due to a reduced Debye temperature, as well as to a possible reduction of anisotropy-effects by an increase of impurity scattering.

References