X-ray and $^{237}$Np Mössbauer effect investigation on the NpB$_2$C compound

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Abstract. Powder x-ray diffraction and $^{237}$Np Mössbauer effect measurements were performed on NpB$_2$C crystallizing in the ThB$_2$C – type structure, $R3m$. On the base on $^{237}$Np Mössbauer spectroscopy formal +3 oxidation states were assigned to both Np sites, 3a and 6c. The magnetic ordering of the Np sublattice below 80 K is confirmed and the value of the ordered moment amounts to 0.30 $\mu_B$ and 1.05 $\mu_B$ on the 3a and 6c Np sites, respectively. The reduced magnitudes of the ordered moment and of the isomer shift suggest rather delocalized 5f electrons.

1. Introduction

The combination of rare earth or actinide metal with boron and carbon atoms leads to the formation of layered compounds having interesting structural and physical properties: superconductivity was observed in YB$_2$C$_2$ and LuB$_2$C$_2$ [1], antiferroquadrupolar (AFQ) and antiferromagnetic (AFM) ordering was reported in DyB$_2$C$_2$ and HoB$_2$C$_2$, respectively [2]. Mostly metallic behaviour for rare earth (actinide) borocarbide compounds was suggested [3;4].

The layered borocarbide compounds with general formula RB$_2$C form metallic and boron-carbon sheets and can crystallize in three different crystal structures: YB$_2$C$_2$, ThB$_2$C$_2$ and $\alpha$-UB$_2$C$_2$ type. Light actinide and cerium borocarbides mostly crystallize in the ThB$_2$C type structure, whereas other rare-earths borocarbides crystallize rather in the two other types of structure. Extended Hückel tight-binding calculations based on an ionic interaction between the metallic and the boron-carbon sublattices assigned a formal charge of -4 per B$_2$C unit to the ThB$_2$C and $\alpha$-UB$_2$C type structures and a formal charge -3 to the YB$_2$C type [3]. In this view, the formation of YB$_2$C type structure is preferred by most of rare earth atoms but the ThB$_2$C type for light actinide and Ce atoms. $\beta$-UB$_2$C with ThB$_2$C type was shown to order ferromagnetically below 74.5K with itinerant nature of the 5f-electrons [5].

NpB$_2$C crystallizes in the rhombohedral space group $R3m$ (No. 166), with the ThB$_2$C-type structure ($a = 6.532(2)$ Å, $c = 10.769(3)$ Å [6,7]). The crystal structure has been derived from single crystal data.
(R$_f$=0.023) and confirms full atom order: Np atoms occupy 3a and 6c sites while B and C atoms are located on the 18g and 9d sites respectively. From polycrystalline bulk NpB$_2$C samples, antiferromagnetic ordering below a Néel temperature of 73K is established by magnetization and specific heat measurements [7]. A ferromagnetic signal observed below about 50K in the magnetization curves at low fields is attributed to the presence of ferromagnetic impurities. In the paramagnetic region, the susceptibility follows a modified Curie–Weiss law with an effective moment $\mu_{eff}$ = 1.65 $\mu_B$ much smaller than the free Np$^{3+}$ ion value (2.75 $\mu_B$), and a paramagnetic Curie–Weiss temperature $\theta_p \approx 23K$.

We report here x-ray diffraction results and $^{237}$Np Mössbauer spectroscopy studies.

2. Experimental details

Polycrystalline ingots were obtained by arc melting stoichiometric amounts of the constituent elements under an atmosphere of high purity argon on a water-cooled copper hearth, using a Zr getter alloy. Starting materials were used in the form of pieces as supplied by Merck AG. (boron and graphite), and by LANL electrorefined neptunium 3N metal. In order to ensure homogeneity, the arc melted buttons were turned over and remelted 3 times, with weight losses below 0.5%. The samples were checked by X-ray powder diffraction data (Cu K$_\alpha$ radiation) collected on a Bragg-Brentano Siemens D500 diffractometer using a 2 step size of 0.02 degrees. The diffraction patterns were analyzed by a Rietveld-type profile refinement method using the Fullprof program [8].

The $^{237}$Np Mössbauer spectra were taken between 4K and 120K in a transmission geometry spectrometer with ~ 100mCi $^{241}$Am source kept at temperature around 4K. The absorber was prepared by grinding the sample to a fine powder to ensure a constant surface density with an optimal thickness of 140mg Np cm$^{-2}$. The velocity scale was calibrated with the NpAl$_2$ compound. The isomer shift, IS, is given relative to NpAl$_2$ at 4K. The spectra were analyzed using Lorenzian lines. The position and relative intensities of the absorption lines of Np nuclei were calculated by solving the complete Hamiltonian for the hyperfine interactions in both the excited and ground nuclear state of $^{237}$Np.
3. Results and discussion

The X-ray diffraction pattern recorded on a polycrystalline sample confirms crystal symmetry, atom occupation and thus isotypism with the crystal structure of ThB\(_2\)C. However, the small disagreement between calculated and experimental peak intensity and broadening suggest texture effects. It could also indicate a small shift of Np atoms from their position induced by vacancies at B or/and C sites. Mössbauer spectra of NpB\(_2\)C at 4K and 120K are presented on Fig. 1.

The two non-equivalent Np sites of NpB\(_2\)C, 3a and 6c, have each 8 Np atoms near neighbors (NN): Np atoms at the 3a site have 8 Np NN at the 6c site within a distance of 3.77Å. Np atoms at the 6c site have 4 Np NN at the 3a site but also 4 Np NN at the 6c site (3 of them within 3.78Å and one within 3.24Å). Thus the model used to account for the Mössbauer spectra contains two components, with relative intensities 1:2. However, this model appears insufficient to fully reproduce the Mössbauer pattern, possibly due to vacancies in the B and/or C sites. Unfortunately, it is not possible from X-rays to establish the exact site occupation of B and C atoms, due to their very low scattering factor compared to Np atoms. Therefore, it is also not possible to build an exact physical model to fit the Mössbauer spectra. The solution could be to fit rather sharp spectra with a distribution of \(^{237}\text{Np}\) hyperfine parameters. As we have no program for fitting a distribution of Np hyperfine parameters we decided to split each Mössbauer spectral component into 3 additional ones for each (3a and 6c) crystallographic site. Only the quadrupole splitting (QS) and the magnetic hyperfine field \(B_{hf}\) were allowed free variation for each of the 6 components. The isomer shift (IS) was kept equal for the three components of a same crystallographic site. During the fitting procedure the linewidth of all lines was constrained to a unique value. The parameters obtained are presented in Table 1. An average value of the quadrupolar interaction parameter and of the hyperfine magnetic field is also given.

| site | T [K] | IS [mm/s] | QS [mm/s] | <QS> | B [T] | <B> [T] | A [%] | <A> [%] |
|------|-------|-----------|-----------|-------|-------|---------|-------|---------|
| 3a   | 4     | 9.8       | 32.0      | 33.2  | 29    | 65      | 11    | 33      |
|      |       |           | 38.0      |       | 69    |         | 11    |         |
|      | 120   | 9.8       | 32.0      | 33.2  | 0     | 0       | 11    | 33      |
|      |       |           | 38.0      |       | 0     |         | 11    |         |
| 6c   | 4     | 0.1       | -16.1     | -16.0 | 240   |         | 13    | 67      |
|      |       |           | -16.2     |       | 210   | 225     |       |         |
|      |       |           | -15.0     |       | 180   |         | 10    |         |
|      | 120   | 0.1       | -16.1     |       | 0     |         | 13    | 67      |
|      |       |           | -16.2     |       | 0     |         |       |         |
|      |       |           | -15       |       | 0     |         |       |         |

Following the value of IS we assigned a formal +3 oxidation state for both Np sites [9]. This formally disagrees with idea of metal atom on formal +4 oxidation state in the ThB\(_2\)C – type structure suggested in ref. 3. However, the relatively low value of IS which is only slightly higher than for Np\(^{+4}\) could indicate Np atoms at an intermediate valence state. The lower magnitude of IS than for Np\(^{+3}\) ion could be explained by hybridization between Np 5f electrons and conduction bands. This leads to a decrease of f-electron density and to an increase of conduction electron density. Both effects are responsible for decreasing IS at the Np site.

The temperature dependences of \(B_{eff}\) at 3a and 6c sites are presented on Fig. 2. Magnetic ordering below 80K is proven. Using the Dunlap-Lander [10] relation we can assign at 4K \(0.30 \mu_B\) and \(1.05 \mu_B\) to the Np 3a and 6c sites, respectively. These values are much lower than the theoretical values for free Np\(^{+3}\) or Np\(^{+4}\) ions [9]. At first glance the higher magnetic moment at 6c could be explained by a lower mean value of interatomic distances, \(d_{\text{Np-Np}}\) for 6c than for the 3a site. However, the huge difference in \(B_{eff}\) at both crystallographically quite similar sites should have its origin in the electronic

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Table 1. Estimated Mössbauer hyperfine parameters for NpB\(_2\)C
structure. In Np intermetallics orbital magnetism is dominant, thus a decreasing f-electron density leads to decreasing magnetic moments on Np atoms. Therefore a lower magnitude of IS shift should be connected with lower B_{eff}. In NpB₂C site 6c has lower IS and higher B_{eff}. It could be understood if we assume hybridization between f, d and s Np electron density with p electron density of B and C atoms leading to the formation of electronic bands responsible for a rather itinerant than localized magnetism in NpB₂C similar to the isotypic itinerant ferromagnet β-UB₂C [5].

4. Summary
X-ray diffraction confirms site occupation and formation of a ThB₂C type structure in NpB₂C. However, the polycrystalline sample contains inhomogeneities, mostly in B and C sites.

\(^{237}\)Np Mössbauer spectra indicate a formal 3+ charge state for Np, but intermediate valence cannot be excluded. Magnetic ordering of both sublattices below 80K is established, with an ordered moment of 0.30 \(\mu_B\) and 1.05 \(\mu_B\) on the Np 3a and 6c sites, respectively. The reduced values (compared to the free ion) of the magnetic moment and the isomer shift suggest (i) hybridization of the 5f Np shell with the conduction band and (ii) rather delocalized 5f magnetism in NpB₂C. These results are in agreement with previous work [7].

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References
[1] Sakai T, Adachi G, Shiokawa J 1982 J. Less-Common Met. 84 107
[2] Yamamuchi H, Onodera H, Kaneko K, Tobo A, Ohoyama K, Yamaguchi Y 2001 J. Magn. Magn. Mat. 266-270 1134
[3] Wiitkar F, Kahlal S, Halet J F, Saillard J Y, Bauer J, Rogl P 1994 J. Am. Chem. Soc. 116 251
[4] Wiitkar F, Kahlal S, Halet J F, Saillard J Y, Bauer J, Rogl P 1995 Inorg. Chem. 34 1248
[5] Tran V H, Rogl P, Andre G, Bouree F 2006 J. Phys.-Cond. Mat, 18 703
[6] Rogl P, Beauvy M, Larroque J P 1989 19th Journées des Actinides Madonna di Campiglio Trento, Italy.
[7] Boulet P, Colineau E, Rebizant J, Rogl P, Wastin F 2004 34th Journées des Actinides Heidelberg, Germany.
[8] Rodriguez-Cavajal J 1993 Physica B 192 55
[9] Kalvius G M, Gal J, Asch L, Potzel W 1992 Hyp. Int. 72 77
[10] Dunlap B D, Lander G H 1974 Phys. Rev. Lett. 63 2413