J Supercond Nov Magn (2008) 21: 457–460
DOI 10.1007/s10948-008-0384-2

ORIGINAL PAPER

Superconductivity of $Nb_{1-x}Mg_xB_2$: Impact of Stretched c-Parameter

Monika Mudgel · V.P.S. Awana · G.L. Bhalla · H. Kishan

Received: 30 May 2008 / Accepted: 22 October 2008 / Published online: 6 November 2008

Abstract We have performed a systematic study on the occurrence of superconductivity in $Nb_{1-x}Mg_xB_2$ ($0.0 \le x \le 0.40$). X-ray diffraction and magnetization measurements are carried out to determine the changes in lattice parameters, superconducting transition temperature (T_c) and critical field (H_{c1}). The substitution of Mg at Nb site results in considerable stretching of c-parameter with only a slight change in a parameter. Rietveld analysis on X-ray diffraction patterns gives $a = 3.11$ Å and $c = 3.26$ Å for pure NbB_2 while $a = 3.10$ Å and $c = 3.32$ Å for $Nb_{0.60}Mg_{0.40}B_2$. This increased c-parameter introduces superconductivity in niobium diboride. Magnetization measurements though indicate the absence of superconductivity in NbB_2, the same shows a clear diamagnetic signal at about 10 K for $Nb_{0.60}Mg_{0.40}B_2$ sample. The magnetization $M(H)$ plots exhibit weak superconductivity like hysteresis loops. The stretching of c-parameter from around 3.26 to 3.32 i.e. by 0.06 cannot be explained solely by substitution of Nb by Mg in the lattice. It seems that some Nb deficiencies are introduced in the $Nb_{1-x}Mg_xB_2$ as Mg is not substituted completely at the vacant Nb sites. This could be seen from XRD results, where one can clearly notice the presence of small amount of MgO in $Nb_{1-x}Mg_xB_2$ samples.

Keywords MgB_2 superconductor · NbB_2 · X-ray diffraction · Magnetization · Superconductivity

M. Mudgel · V.P.S. Awana (✉) · H. Kishan
National Physical Laboratory, Dr. K.S. Krishnan Marg,
New Delhi 110012, India
e-mail: awana@mail.nplindia.ernet.in
url: https://www.freewebs.com/vpsawana/

G.L. Bhalla
Department of Physics and Astrophysics, Delhi University,
New Delhi 110007, India

PACS 61.10.Nz · 74.62.-c · 74.62.Bf

1 Introduction

The discovery of superconductivity in MgB_2 [1] has put an impetus in search for analogous behavior in similar systems. Although the most similar candidates for such investigations seem to be the AlB_2 type alkali, alkaline or group III element diborides, i.e., AB_2 (A = Li, Na, Be, Al), none of them is reported to have superconductivity [2–4]. The group IVa, Va & VIIa elements (Nb, Ta, Mo, Zr and Hf) also form diborides isostructural to MgB_2. These transition metal diborides are studied theoretically by various groups [5–7] but the reports on the experimental approach towards the synthesis and characterization of diborides other than MgB_2, are still scant. The superconducting behavior of diborides like ZrB_2, NbB_2, and TaB_2 has been a matter of debate for many years. ZrB_2 is reported to have superconductivity by Gasprov et al. [8] while Leyrovska and Leyrovski [9] report no superconductivity in this compound. Similar controversial reports exist on TaB_2 and NbB_2 [8–12]. Hulm and Mathias and others [13, 14] reported superconductivity in boron deficient alloys like $NbB_{1.94}$. Also Cooper et al. [15] found superconductivity in Nb-deficient compositions, such as $NbB_{2.5}$, but absence of superconductivity in stoichiometric NbB_2. On the other hand, several reports exist on the presence of superconductivity in stoichiometric NbB_2 with different transition temperatures [16–19].

MgB_2 is a superconductor with quite high T_c of 39 K. The reason behind its high T_c, unlike other diborides, is its light constituents Mg and B and the stretched c-parameter. The c/a value of MgB_2 is 1.14 while for pure NbB_2 it is 1.05. The introduction of superconductivity in NbB_2 by increasing c-parameter is reported in literature [20, 21] as well as in one of our papers [22] mainly in Nb-deficient case. Keeping this key point in mind, we have synthesized $Nb_{1-x}Mg_xB_2$ samples by simple solid-state reaction route at ambient pressure in order to induce an increase in c-parameter. The structural and superconducting characterization is carried out systematically for all the samples. The impact of Mg substitution at Nb site on the superconducting parameters like transition temperature (T_c) and critical field (H_{c1}) is studied in detail.

2 Experimental

Polycrystalline bulk samples of $Nb_{1-x}Mg_xB_2$ were synthesized by solid-state reaction route. The commercially available NbB_2 and MgB_2 powders were taken in stoichiometric ratios and were well mixed by continuous grinding. The uniformly mixed powders were palletized using a hydraulic press applying a pressure of 8 ton/cm^2. The pellets were enclosed in soft iron tubes and then sealed in Quartz tube up to a vacuum of 10^{-5} torr. The sealed quartz tubes were sintered at 1100°C for 20 hours followed by natural cooling to room temperature. The heating rate was about 550°C per hour. X-ray diffraction patterns were recorded for all the samples on Rigaku ultima Miniflex-II at room temperature. The phase purity was confirmed by Rietveld refinement on the X-ray diffraction profiles. Magnetic measurements were performed on Quantum designed SQUID magnetometer (*MPMS-XL*).

3 Results and Discussion

The X-ray diffraction patterns for the pure and Mg-substituted NbB_2 samples are shown in Fig. 1. The characteristic peaks for pure NbB_2 sample are indexed in the figure. No impurity peak of considerable intensity is noticed. NbB_2 crystallizes in AlB_2 type hexagonal structure in the space group *P6/mmm*. The Mg-substituted samples are also phase-pure except for a small-intensity MgO peak. A shift in the (002) peak towards the lower angle side with increasing Mg content is shown (marked with *) clearly in inset of Fig. 1. The MgO formation in Mg-substituted samples confirms the creation of metal vacancy up to some extent in the NbB_2 lattice. In order to confirm the exact phase formation and to determine the lattice parameters precisely, the Rietveld analysis is done on all the samples.

Figure 2(a) shows the observed and fitted pattern for pure NbB_2. The atomic positions taken are Nb (0, 0, 0) and B (1/3, 2/3, 1/2) in *P6/mmm* space group (No. 191). There is a close agreement between the experimentally observed (shown by dots) and the theoretical Rietveld generated pattern (shown by line). The difference between the two is drawn at the bottom. The Bragg positions are also marked above the difference line. All expected Bragg reflections are obtained without any extra impurity line. The lattice parameters for pristine NbB_2 sample are $a = 3.11002(8)$ Å and $c = 3.26453(11)$ Å with c/a value of 1.05. In order to speculate about the changes in the lattice parameters with Mg content, Rietveld analysis for Mg-substituted samples is also done. Figure 2(b) depicts the Rietveld analysis of $Nb_{0.60}Mg_{0.40}B_2$ sample. The presence of small MgO impurity is marked on the pattern. Again we see that there is hardly any difference between the observed and theoretical curves. The lattice parameters are $a = 3.10003(14)$ Å and $c = 3.31994(11)$ Å. The lattice parameters, c/a value, as well as cell volume for all studied $Nb_{1-x}Mg_xB_2$ ($x = 0.0$ to 0.40) are tabulated in Table 1. Both a and c parameters change monotonically with the Mg content. The parameter a decreases slightly but c-parameter undergoes a sharp increase with Mg content. c/a value also increases continuously indicating that lattice is stretched in c-direction. The monotonic changes in lattice parameters are in confirmation with the only earlier report on $Nb_{1-x}Mg_xB_2$ [23].

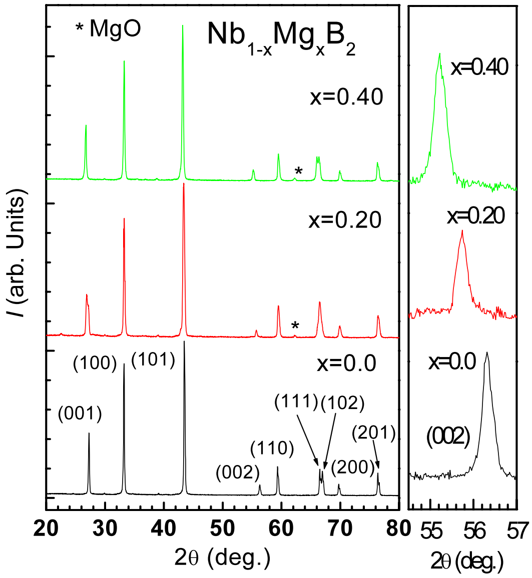
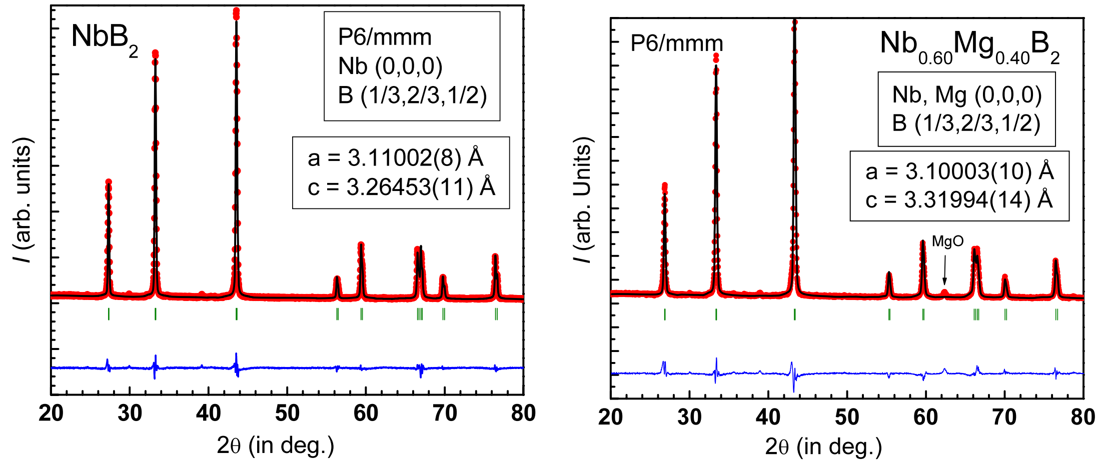


Fig. 1 X-ray diffraction patterns of $Nb_{1-x}Mg_xB_2$ ($x = 0.0$, 0.20 and 0.40) samples in the angular range $20° \leq 2\theta \leq 80°$. *Inset* shows the enlarged view of shift in (002) peak. The MgO impurity is marked with *

Magnetic susceptibility variation with temperature (M–T) for $Nb_{1-x}Mg_xB_2$ samples is shown in Fig. 3. Pure NbB_2 sample does not show any diamagnetic signal down to 5 K. The superconductivity is introduced with the Mg substitution in the NbB_2 lattice. $Nb_{0.80}Mg_{0.20}B_2$ shows a clear diamagnetic signal at transition temperature of about 9.5 K in zero-field-cooled measurement. Transition temperature increases with the increase in Mg content. For $Nb_{0.60}Mg_{0.40}B_2$ sample, T_c is maximum, i.e. 10 K. The inset shows the field-cooled and zero-field-cooled magnetiza-



(a) (b)

Fig. 2 Rietveld refined plots for **a** NbB_2 and **b** $Nb_{0.60}Mg_{0.40}B_2$ samples. X-ray experimental diagram (*dots*), calculated pattern (*continuous line*), difference (*lower continuous line*) and calculated Bragg position (*vertical lines in the middle*)

Table 1 Rietveld refined parameters for $Nb_{1-x}Mg_xB_2$ samples ($x = 0.0 - 0.40$)

Sr. No.	x in $Nb_{1-x}Mg_xB_2$	a (Å)	c (Å)	c/a	Volume (Å^3)
1	0.0	3.11002(8)	3.26453(11)	1.050	27.345(1)
2	0.20	3.10260(21)	3.29470(26)	1.062	27.466(3)
3	0.40	3.10003(11)	3.31994(14)	1.071	27.631(2)

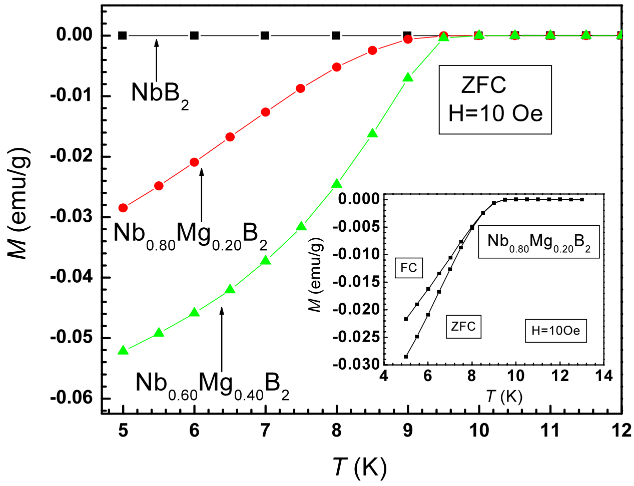


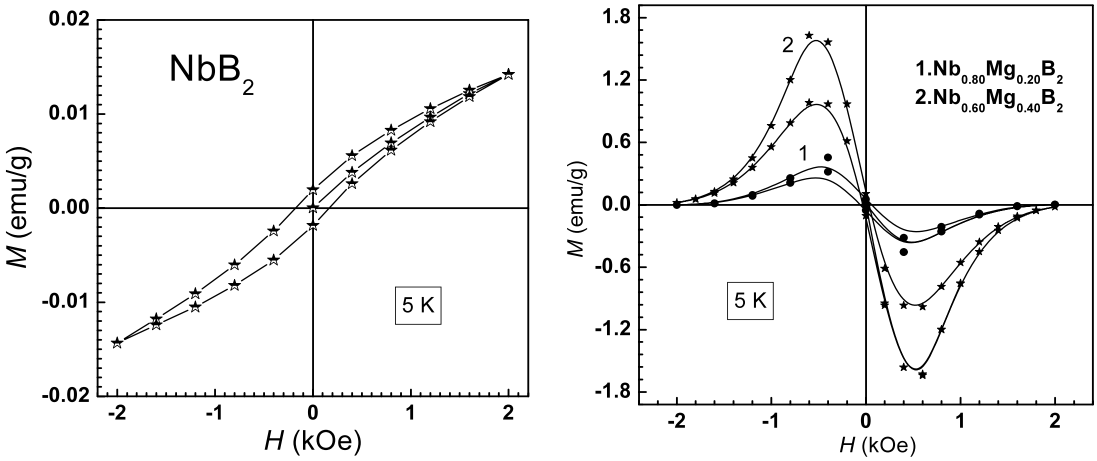
Fig. 3 Magnetization–temperature measurements showing the transition temperature for $Nb_{1-x}Mg_xB_2$ samples with $x = 0.0$, 0.20 and 0.40. *Inset* shows the FC and ZFC magnetization plots for $Nb_{0.80}Mg_{0.20}B_2$ sample

tion curves for $Nb_{0.80}Mg_{0.20}B_2$ sample. In both the situations, the diamagnetic signal is obtained at the same temperature $T_c^{\mathrm{Dia}} = 9.5$ K.

Magnetic measurements (M–H) are also taken with the varying field at a fixed temperature of 5 K in both increasing and decreasing directions. The M–H hysteresis loop for pristine NbB_2 sample is shown in Fig. 4(a). The sample is slightly paramagnetic and has a magnetic hysteresis with respect to the direction of the field. Paramagnetic nature at 5 K again confirms the absence of superconductivity in this sample. Figure 4(b) depicts the M–H curves for Mg-substituted NbB_2 sample. As we can see in the IVth quadrant, the diamagnetic moment develops with the increasing field and reaches the maximum at a field value, H_{c1}, of about 465 and 520 Oe for $x = 0.20$ and 0.40 samples, respectively. With the further increment in the field, the diamagnetic moment begins to gradually decrease, as generally happens in Type-II superconductors. The diamagnetic signal vanishes at a field value of about 2000 Oe, i.e. the sample remains no longer superconducting with the further increase in the field. The magnitude of diamagnetic moment for $Nb_{0.60}Mg_{0.40}B_2$ sample is more than four times that of $Nb_{0.80}Mg_{0.20}B_2$ sample at its peak, which shows an improved superconductivity with increasing Mg content.

4 Conclusion

The impact of Mg substitution at Nb site is studied on the structural and superconducting properties of niobium diboride. Mg substitutes at Nb site up to 40%. It results into a sharp increase in c-parameter, while a slight decrease in a-parameter. This lattice stretching brings about superconductivity in niobium diboride in the same way as in NbB_{2+x}



(a) (b)

Fig. 4 Magnetization hysteresis loops (M–H) for **a** pure NbB_2 sample **b** Mg-substituted niobium boride samples at 5 K

case. Pure stoichiometric NbB_2 is a non-superconductor while both Mg-substituted samples possess superconductivity. The superconducting transition temperature (T_c) and critical field value (H_{c1}) increase with the increase in Mg content.

Acknowledgements The authors from *NPL* would like to thank Dr. Vikram Kumar (Director, *NPL*) for showing his keen interest in the present work. One of us, Monika Mudgel, would also thank *CSIR* for financial support by providing *JRF* fellowship. Authors would also like to thank Prof. E. Takayama-Muromachi from *NIMS* Japan for providing us with the *SQUID* magnetization measurement facility.

References

1. Nagamatsu, J., Nakagawa, N., Muranaka, T., Zenitani, Y., Akimitsu, J.: Nature **410**, 63 (2001)
2. Slusky, J.S., Rogado, N., Regan, K.A., Hayward, M.A., Khallfah, P., He, T., Innumaru, K., Loureiro, S.M., Haas, M.K., Zandbergan, H.W., Cava, R.J.: Nature **410**, 343 (2001)
3. Felner, I.: Physica C **353**, 11 (2001)
4. Zhao, Y.G., Zhang, X.P., Qiao, P.T., Zhang, H.T., Jia, S.L., Cao, B.S., Zhu, M.H., Han, Z.H., Wang, X.L., Gu, B.L.: Physica C **361**, 91 (2001)
5. Jariwala, C., Chainani, A., Tsuda, S., Yokoya, T., Shin, S., Takano, Y., Togano, K., Otani, S., Kito, H.: Phys. Rev. B **68**, 174506 (2003)
6. Shein, I.R., Ivanovski, A.L.: cond-mat/0109445 (2001)
7. Kolmogorov, A.N., Curtarolo, S.: cond-mat/0607545 (2006)
8. Gasprov, V.A., Sidorov, N.S., Zever'kova, I.I., Kulakov, M.P.: JETP Lett. **73**, 601 (2001)
9. Leyarovska, L., Leyarovski, E.: J. Less-Common Met. **67**, 249 (1979)
10. Rosner, H., Pickett, W.E., Drechsler, S.L., Handstein, A., Behr, G., Fuchs, G., Nankov, K., Muller, K.H., Eshrig, H.: Phys. Rev. B **64**, 144516 (2001)
11. Yamamoto, A., Takao, C., Matsui, T., Izumi, M., Tajima, S.: Physica C **383**, 197 (2002)
12. Kaczorowski, D., Zaleski, A.J., Zogal, O.J., Klamut, J.: cond-mat/0103571 (2001)
13. Hulm, J.K., Mathias, B.T.: Phys. Rev. **82**, 273 (1951)
14. Zeigler, W.A., Young, R.: Phys. Rev. **94**, 115 (1953)
15. Cooper, A.S., Corenzwit, E., Longinotti, L.D., Mathias, B.T., Zachariasen, W.H.: Proc. Natl. Acad. Sci. **67**, 313 (1970)
16. Kotegawa, H., Ishida, K., Kitaoka, Y., Muranaka, T., Takagiwa, H., Akimitsu, J.: Physica C **378**, 25 (2002)
17. Schriber, J.E., Overmeyer, D.L., Morosin, B., Venturini, E.L., Baughman, R., Emin, D., Klesnar, H., Aselage, T.: Phys. Rev. B **45**, 10787 (1992)
18. Hulm, J.K., Mathias, B.T.: Phys. Rev. B **82**, 273 (1951)
19. Zeigler, W.A., Young, R.: Phys. Rev. B **94**, 115 (1953)
20. Ren, Z.A., Kuroiwa, S., Tomita, Y., Akimitsu, J.: Physica C **468**, 411 (2008)
21. Escamilla, R., Lovera, O., Akachi, T., Duran, A., Falconi, R., Morales, F., Escudero, R.: J. Phys.: Condens. Matter **16**, 5979 (2004)
22. Mudgel, M., Awana, V.P.S., Bhalla, G.L., Kishan, H.: Solid State Commun. **147**, 439 (2008)
23. Geng, H.X., Che, G.C., Huang, W., Jia, S.L., Chen, H., Zhao, Z.X.: Supercond. Sci. Technol. **20**, 452 (2007)