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Relationship between superconductivity and crystal structure in NbB\(_2+\_x\)

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Abstract

We have performed magnetic susceptibility measurements and precise crystal structure analysis of the nonstoichiometric NbB\(_{2+x}\) superconductor to reveal the relationship between \(T_c\) and crystal structure. From magnetic susceptibility measurements, it was found that \(T_c\) increases from 2.2 to 5.8 K with \(x\). The crystal structures including both chemical compositions and lattice constants were precisely determined by Rietveld refinement using synchrotron X-ray powder diffraction data with three different wavelengths. We found that interatomic Nb–B distance increases with \(T_c\). The charge density of NbB\(_{2+x}\) was revealed by the maximum entropy method based on Rietveld refinement. We find the difference in the number of electrons in the Nb site and B layer for NbB\(_{2+x}\), with different compositions and \(T_c\).

Keywords: Superconductivity; NbB\(_2\); Maximum Entropy Method (MEM)

1. Introduction

After the discovery of superconductivity in MgB\(_2\) [1], a large number of theoretical and experimental studies of this material were performed. This material has an AlB\(_2\)-type structure with a space group of \(P6_3/mmm\) and consists of a stacking layer along the \(c\)-axis with metal atoms of triangular and honeycomb networks of boron atoms. Theoretical calculations and experimental studies suggest that this two-dimensional network formed by boron atoms is responsible for the appearance of high-\(T_c\) superconductivity in MgB\(_2\). Chemical substitutions on Mg- and B-sites have also been carried out to understand the effect of the carrier concentration on \(T_c\). For example, several substitution experiments have been reported for Mg\(_{1-x}\)Al\(_x\)B\(_2\) [2], Mg\(_{1-x}\)Mn\(_x\)B\(_2\) [3], MgB\(_{2-x}\)C\(_x\) [4] and MgB\(_{2-x}\)Be\(_x\) [5]. High-pressure studies on MgB\(_2\) have also been performed and discussed for the Mg–B and B–B bonding distances and for the relationship between \(T_c\) and cell volume [6,7]. All experiments reported a decrease in \(T_c\) for any chemical substitutions on Mg- and B-sites. On the other hand, the hexagonal diborides MB\(_2\), where M is a metal element, have been compared with that of MgB\(_2\). Although the superconductivities of TaB\(_2\) [8], ZrB\(_2\) [9] and BeB\(_2\) [10] have been reported, reproducibility and impurity problems still remain for TaB\(_2\) and ZrB\(_2\), and the crystal structure of BeB\(_2\) is different from that of the AlB\(_2\) type, and the physical properties of this material are difficult to measure because of its low \(T_c\) (\(T_c=0.72\) K).

The superconductivity of NbB\(_2\) has been well known since the 1970s. For example, Cooper et al. reported in 1970 [11], the superconductivity of NbB\(_2\) with a boron-rich composition (\(T_c=3.87\) K), however, Leyarovska et al. showed in 1979 [12] that stoichiometric NbB\(_2\) has a lower \(T_c\) (\(T_c=0.62\) K). Schirber et al. reported \(T_c=9.4\) K in a single-crystal sample of NbB\(_x\) (\(x\approx 2\)) [13]. Therefore, the \(T_c\)'s of NbB\(_2\) are closely related to the Nb and boron ratio. Recently, Yamamoto et al. have reported the superconductivity and lattice parameters of Nb\(_{1-x}\)B\(_x\) (\(x=0-0.48\)) prepared under a high pressure [14]. However, the precise crystal structure and its relationship to the superconductivity in nonstoichiometric NbB\(_{2+x}\) have not been reported. In this letter, we present the superconductivities and precise crystal structures of NbB\(_{2+x}\), having different nominal compositions and \(T_c\)'s, using synchrotron radiation powder data. Moreover, the charge density determined by the combination of the maximum entropy method (MEM) and Rietveld refinement, what we call the MEM/Rietveld method [15,16], indicates a definite difference in the number of electrons in the Nb site and B layer for NbB\(_{2+x}\), with different compositions and \(T_c\).
electrons in the Nb site and B layer for NbB$_{2+x}$ with different ratios of Nb and B.

2. Experimental details

The polycrystalline samples of NbB$_{2+x}$ used in this study were synthesized from Nb (99.5%) and boron crystalline powders (99%). The pellets of these mixtures were sealed using a quartz tube at vacuum pressure and heated at 1000°C for 30 h. The synthesized samples are called sample nos 1–5 for different content ratios of B/Nb. The nominal compositions for each sample are listed in Table 1. The magnetic susceptibilities were measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). To investigate the crystal structure-$T_c$ relationship, the synchrotron radiation X-ray powder pattern experiments with an imaging plate as detectors were performed using a large Debye–Scheerer camera at Spring-8, BL02B2.

3. Experimental results and discussion

Fig. 1 shows the temperature dependence of field-cooling magnetic susceptibilities at 10 Oe for sample nos 1–5. Diamagnetic signals with the Meissner effect can be observed and the superconducting volume fractions are calculated to be about 40% for all samples without sample no. 1. For sample no. 1, it is only $\ll$1% at 1.8 K, which is the limit of our system because of its low-$T_c$. These data indicate that these superconductivities are due to bulk nature. Moreover, these have different $T_c$ values from 2.2 to 5.8 K, which increase with $x$.

The synchrotron radiation X-ray powder patterns were measured for sample nos 1–5 at 300 K. The wavelengths of incident X-rays were 0.654, 0.656 and 0.660 Å. The exposure time was 35 min for each sample. Fig. 2 shows powder patterns for sample nos 1–5. We obtained the profiles of the AlB$_2$-type structure with no superlattice reflection and no other structure except for sample no. 1. In the powder pattern for sample no. 1, the weak impurity peaks were observed at a low angle. This impurity phase was eliminated from the data by profile fitting preanalysis. We found that the powder profiles of 001 reflections shift systematically with increasing $x$. In the inset of Fig. 2, the peaks of 003 reflections significantly shift to a lower angle as indicated by arrows. Moreover, the peaks of 210 reflections shift to a higher angle and those of 103 reflect shift to a lower angle, and these two peaks crossover at sample no. 2 and distance between both peaks increases with $x$.

We have performed Rietveld refinement to determine the precise crystal structure of sample nos 1–5. The lattice constants determined by Rietveld analysis are listed in Table 1. The cell volumes of each sample calculated from the lattice constants are plotted in Fig. 3. In sample nos 1, 2 and 3, the volume increases with increasing boron content. On the other hand, the volume decreases with increasing boron content in sample nos 4 and 5. It was found that sample no. 3 has a maximum volume. For this result, we considered sample nos 1, 2 and 3 to be boron deficient, and sample nos 4 and 5 to be Nb deficient. Therefore, we refined the occupancy of atoms in Rietveld refinement to deal with the deficiencies of Nb and B atoms. From the nominal composition, the occupancy factor of boron atoms was refined in sample nos 1, 2 and 3 and the occupancy factor of Nb atoms was refined in sample nos 4 and 5. The determined compositions by Rietveld analysis were listed in Table 1. The reliability factors of the Rietveld refinements based on the weighted profile $R_{WP}$, and based on the Bragg intensities $R_I$, were as small as in the ranges from 2.1 to 2.5.

![Fig. 1. Temperature dependence of field cooling susceptibilities for NbB$_{2+x}$.](image-url)
to 2.5% and from 0.9 to 1.2%. Furthermore, the determined parameters were confirmed by the Rietveld refinements of two other different wavelength data, 0.656 and 0.660 Å. The B/Nb ratios from Rietveld refinement shifted from the nominal one with $x$. The largest shift was found in sample no. 5 where Nb$_{B2.4}$ became Nb$_{0.968(2)}$B$_2$. This result indicates that boron is hardly soluble for nonstoichiometric NbB$_2$.

We also examined the charge density distribution of sample nos 2 and 5 by the MEM/Rietveld method. The MEM calculation was carried out using the computer program ENIGMA [17]. A three-dimensional representation of the MEM charge density for sample no. 2 is shown in Fig. 4 as an equicharge density surface. The equidensity level is 1.15 e/Å$^3$. The obtained MEM charge density shows no localized electron density peaks between Nb and boron atoms, suggesting that there are no interstitial boron sites. We also found the covalent bonding nature of boron atoms forming a two-dimensional honeycomb network and the ionized Nb atoms, which have no overlapping of the charge density with neighboring atoms.

In Fig. 5, the MEM charge densities of the 110 sections containing Nb and boron atoms are shown for sample no. 2 at 300 K. The charge density at the Nb–boron midpoint is 0.88 e/Å$^3$, which is much larger than that of MgB$_2$ [18], 0.16 e/Å$^3$, suggesting that covalent interactions between boron and Nb layers increase because of the hybridization of B$_2p$–Nb$_4d$ states. Moreover, Fig. 6 shows the $T_c$ dependence of the Nb–B bonding distance $d_{Nb-B}$ for NbB$_{2+x}$. $T_c$ linearly increases with $d_{Nb-B}$. Therefore, we conclude that the hybridization of B$_2p$–Nb$_4d$ states becomes weaker with increasing $d_{Nb-B}$ and thus $T_c$ increases.

On the other hand, the valence of the atom was examined by determining the number of electrons around a certain atom on the basis of MEM density. The numbers of electrons around Nb atoms are estimated as about 37 and 35.9 e for sample nos 2 and 5, respectively. These values show that the Nb atoms become Nb$_{4+}$ ions for both sample nos 2 and 5. For sample nos 2 and 5, the charge density values at the boron–boron bonding midpoints are 1.18 and 1.08 e/Å$^3$ and the number of electrons contained in the boron layers are 10.085 and 9.418 e, respectively. This fact indicates that $T_c$ is higher in the case of small electrons in the two-dimensional boron sheet for NbB$_{2+x}$ at 300 K. Although, in NbB$_2$, it is reported that the sign of the Hall coefficient $R_H$ is negative [19], i.e. the carrier is an electron. Therefore, since the electron doping of sample no. 5 is caused by the deficiency of Nb atoms, it is considered that the $T_c$ of sample no. 5 is higher than that of sample no. 2.
4. Summary

In summary, we have performed magnetic susceptibility measurements and synchrotron radiation X-ray experiments to reveal the relationship between $T_c$ and the crystal structure of NbB$_2$C$_x$. The precise crystal structures were presented for NbB$_2$C$_x$, which have different $T_c$ values, and we found that $T_c$ increases linearly with $d_{\text{Nb-B}}$. By the MEM/Rietveld method, the spread of the electric charge distribution between boron atoms and Nb atoms was shown. Moreover, we found a difference in the numbers of the electrons around Nb atoms and boron layers in NbB$_2$C$_x$, which have different $T_c$ values. By the present study, it is revealed that the carrier density and/or the hybridization of B$_2p$–Nb$_4d$ states plays an important role in the superconductivity of this material.

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