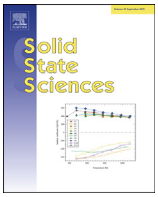
Solid State Sciences 47 (2015) 7–12

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie



# Fe-doped β-Rhombohedral boron: Structural changes at the p-type/n-type transition

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ARTICLE INFO

*Article history:*
Received 30 September 2014
Received in revised form
18 November 2014
Accepted 21 November 2014
Available online 22 November 2014

*Keywords:*
Beta-rhombohedral boron
Fe-doping
Phonon spectra
p/n transition

ABSTRACT

n-type β-rhombohedral boron is e.g. obtained by interstitial doping with Fe atoms exceeding 2.45 at.%. The spectra of Raman- and IR-active phonons have been measured up to the solubility limit of ~4 at.%. Numerous significant discontinuities in the spectra indicate structural changes at the p/n-transition. These might be restricted to specific elements of the structure, as the lattice parameters vary continuously, thus indicating that the overall structure remains largely unchanged.

## 1. Introduction

Pure β-rhombohedral boron is a p-type semiconductor. Fe atoms, interstitially distributed in voids of the open structure, were the first dopant yielding n-type conductivity [1]. Meanwhile, very low V, Cr, and Ni contents have been found to generate extraordinary high negative Seebeck coefficients at ambient conditions [2–5]. Contrary to classical semiconductors, this doping is not simply due to a charge transfer from the dopant to the basic structure, finally overcompensating the acceptor states in the band gap. As outlined by Werheit [6], a correlation between the *3d*-atoms accommodated in specific interstitial sites is to be assumed; and the conductivity character changes, when the concentration exceeds a critical value.

Fe-doped β-rhombohedral boron has been investigated in some detail [7–10]. Below, we present and discuss the spectra of Raman - and IR -active phonons, indicating that the p/n-transition (transition from p-type to n-type conductivity at ~2.44 at.% Fe-content) is accompanied by structural changes. For the Raman spectra of high-purity β-rhombohedral boron see [11] for the IR spectra see [16] and references therein. The effect of isotopes in the phonon spectra of β-rhombohedral boron are discussed in [12].

## 2. Structure

The idealized structure of β-rhombohedral boron $(B_{12})_4(B_{28})_2B$ (for structure models see e.g. [15–17]) has a deficiency of 5 electrons per unit cell. This is compensated by structural defects in terms of incompletely occupied regular boron sites B(13) and B(16)–B(20). These defects evoke intrinsic electronic gap states, split-off from the valence band and leaving the remaining valence band completely occupied [13]. Recently, Ogitsu et al. [14,15] attributed the defect structure of β-rhombohedral boron to a geometrical frustration. They show that the atomic sites related form a double layer-expanded kagome lattice.

The actual crystal structure of β-rhombohedral boron (see e.g. [16] and references therein) containing ~106.7 boron atoms per rhombohedral unit cell consists of the following structure elements:

1 $B_{12}$ icosahedron at each vertex (1 × 12 atoms per unit cell)
1 $B_{12}$ icosahedron at each edge centre (3 × 12 atoms per unit cell)
1 B atom in the center of the unit cell (1 atom per unit cell).

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http://dx.doi.org/10.1016/j.solidstatesciences.2014.11.010
1293-2558/

2 $B_{28}$ units symmetrically accommodated on the main diagonal (2 × 28 atoms per unit cell). 2 × 3 B(13) sites neighbouring the central B; occupancy ~75% (−1.5 atoms per unit cell)
Sites B(14)–B(20), partially occupied; occupancies decreasing from 27.2 to 3.7 % (in total ~ 3.2 atoms per unit cell)

Between the polyhedra, there are large interstitial spaces, named A–F, which enable accommodating foreign atoms, in particular specific metals. Their structural positions and individual environments by boron atoms have been visualized by Hyodo et al. [17]. The occupancies of these sites, depending on the kind and concentration of foreign atoms, are known from structure analysis (see [16] and references therein).

The interstitial sites A–F and the partially occupied boron sites are sometimes close together or they even coincide. This suggests that interstitial doping affects the occupancy of the neighbouring boron sites. Reason could be spatial displacement or charge transfer. Below, the phonon spectra, varying depending on the content of interstitial Fe atoms and apparently restricted to specific structure elements, indicate such structural changes. The coincidence with the change of the conductivity character from p-type to n-type favours charge transfer as the essential reason.

Fe atoms in the β-rhombohedral boron structure are accommodated in the interstitial sites A and D only (for details, see [6]). Maximum solubility is reached at occupancies of two Fe atoms in both kinds of sites per unit cell each. Based on 106.7 B atoms per unit cell, this corresponds to the compound $FeB_{26.6}$ [8]. In both sites, the occupancy increases linearly with the Fe content. Within the accuracy of measurement, the lattice parameters increase linearly as well [1,3,18,19]. As shown in Fig. 1, there is no significant deviation perceptible at the p/n-transition, thus indicating that the overall structure remains largely unchanged. The individual charges of the Fe ions were derived from investigation of the Mössbauer effect [9].

## 3. Samples

Specimens with the nominal chemical compositions $FeB_{1080}$, $FeB_{300}$, $FeB_{110}$, $FeB_{40}$, $FeB_{39.5}$, $FeB_{29.5}$ and $FeB_{24}$ were prepared by arc melting and heat treating at 1470 K (for details, see [8]). $FeB_{40}$ and $FeB_{39.5}$ are particularly important, as these compounds are immediately below and above the p/n-transition respectively. $FeB_{24}$ is close to the solubility limit. As all samples were prepared from the same source materials and in the same procedure, individually varying properties are largely excluded. For comparison, high purity β-rhombohedral boron, obtained by multiple zone melting, (Wacker, Munich, Germany; 99,9999% purity except carbon with typically 60 ppm) was taken.

## 4. Phonon spectra

The Raman spectra (Fig. 2) were obtained at ambient conditions with a Jobin-Yvon Labram 010 spectrometer in backscattering geometry, using the green Ar ion laser line (514.5 nm, 2.410 eV) for excitation; cut-off frequency by an edge filter is ~100 $cm^{-1}$.

MIR/FIR reflectivity spectra were measured with a FT (Fourier transform) IR spectrometer IFS 113v (Bruker) [7,8]. The absorption spectra (Fig. 3) were calculated using the Kramers–Kronig relation.

The Raman spectra below and above the p/n-transition are significantly different, though the lattice parameters (Fig. 1) vary continuously. The frequencies of the Raman-active phonons (Fig. 4) exhibit discontinuities at the p/n-transition. In the IR phonon spectra (Fig. 5) such remarkable discontinuities occur below 400 $cm^{-1}$ only. We note that in the series of IR spectra the $FeB_{39,5}$ sample is missing; therefore in Fig. 5 the data obtained at high Fe contents are extrapolated towards the p/n transition.

Calculated dispersion curves of β-rhombohedral boron are missing so far. Therefore the attribution of phonon peaks in the spectra to specific atomic vibrations is limited to few, empirically determined ranges. Some of them are defined in analogy to the spectra of α-rhombohedral boron (see [11,12]):

(i) Near 1250 $cm^{-1}$: IR-active $A_{2u}$ type vibration of the single B(15) atom in the centre of the unit cell parallel to the crystallographic c-axis (see Fig. 3a). The B(15) atom is symmetrically bonded to 2 × 3 neighbouring B(13) atoms

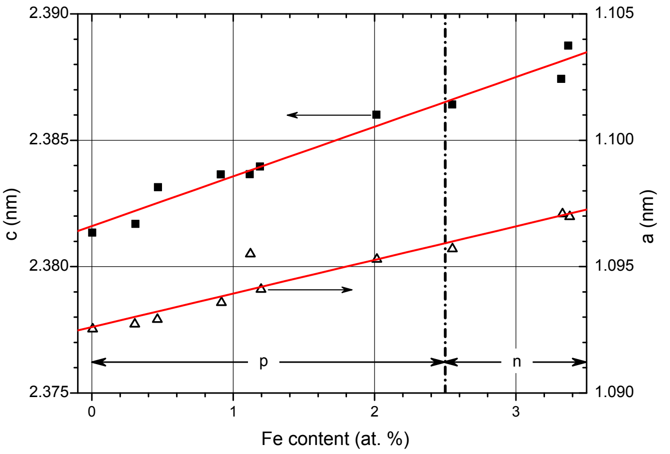

**Fig. 1.** Lattice parameters of Fe-doped β-rhombohedral boron [8]. Dash-dotted line, position of the p/n-transition.

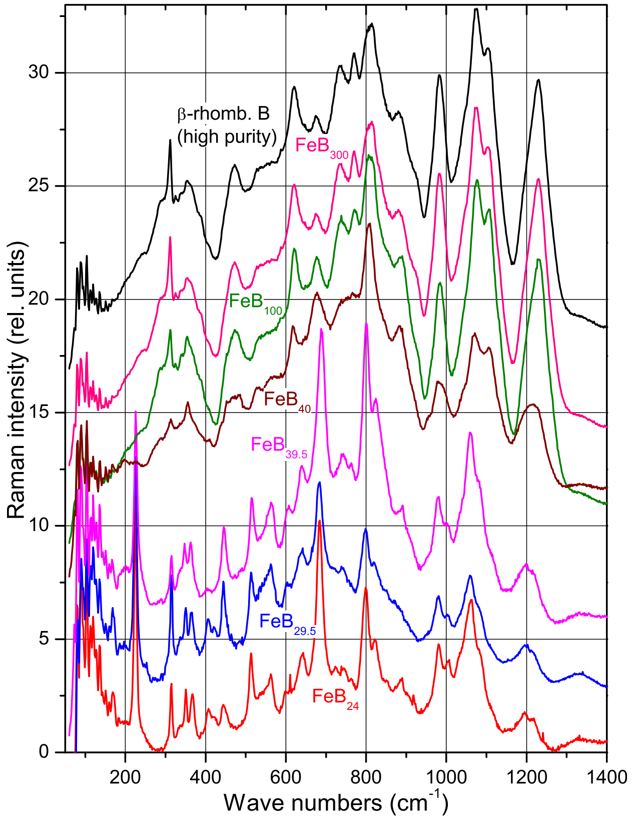

**Fig. 2.** Raman spectra of interstitially Fe-doped β-rhombohedral boron.