Research on superconductivity in α-boron
(αホウ素の超伝導に関する研究)
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Hard materials are considered as candidates for high T_c superconductor. However, many of hard materials are semiconductors, and hence do not exhibit superconductivity. Metallization by some means is required. Boron crystals belong to this category; many efforts have been examined to achieve metallization. In this paper, I have studied theoretically the metallization of α-boron by two different strategies. The one is use of heavy doping and the other is use of high pressure. In both cases, accurate predictions for the electronic structures are required, for which an approach of the materials design by first-principles calculations provides an extremely efficient method.

For the doping strategy, I have examined many dopant impurities through evaluation of the formation energy. The formation energy of impurity atom has been evaluated by modeling a structure as one impurity atom is inserted in the primitive unit cell of α-boron. In most cases, O site is the most stable site. It is found that Li is the best candidate in terms of both the formation energy and the electronic property of rigid band shift. Unfortunately, even though the formation energy of Li is the smallest among those elements so far calculated, the formation energy is still positive, so that heavily doping, which is desirable for superconductivity research, is difficult. In order to overcome this difficulty, we have devised an efficient method to use high pressure. The formation energy is decreased as pressure increases, and eventually becomes negative around 5 GPa. This suggests that doping of Li at pressures higher than 5 GPa is easy.

The above consideration is based on the simplest structural model for the impurity system. When larger supercells are used, further complications arise. Even though our conclusion that O site is the most stable site does not change, there are many impurity configurations whose energy is close to that of O site. This suggests occurrence of disorder in Li position at finite temperatures. The present phonon calculations show that a simple structure of LiB_{12} for which Li is located at O site is dynamically unstable, because of presence of imaginary frequencies. Whether this shows absolute instability of the simple structure LiB_{12} or some structural modifications such as commensurate

structures is not clear at present. Recent discovery of superconductivity for Li-doped α-boron by experimentalists urges us to further study in this system.

For the second approach, a recent experiment shows that α-boron undergoes superconductivity transition (about 5 K) at pressure around 160 GPa. High-pressure experiment shows that the crystal structure of α-boron remains up to 200 GPa. Hence, the metallization must be due to the band overlap within the same structure, which is a rare case for semiconductors. The present calculation shows that the gap closure occurs at 130 GPa. This is consistent with the above experiment. The metallization mechanism is discussed based on the pressure dependence of the band structure. Even for the metallic phase, phonon calculations show that there is no softening, so that the crystal is stable, contrary to the case in Li-doped structure.

The electron-phonon coupling λ has been calculated. For the present case, it is noted that both of the electron and hole bands appear for the Fermi surface, which are far from isotropic. It is found that the effective coupling comes from electrons. The value $\lambda = 0.87$ seems reasonable for the observed $T_c \approx 5$ K, based on the conventional electron-phonon mediated mechanism for superconductivity.