

## PAIRING ENERGY OF LITHIUM AND BORON IN SILICON

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Recent theory<sup>1</sup> and experiment<sup>2-4</sup> have demonstrated that isolated substitutional boron impurities in silicon give rise to an infrared active, local mode of vibration. The room-temperature absorption band for the boron-10 isotope in silicon is at  $644\text{ cm}^{-1}$ . When the silicon samples are well compensated, containing equal concentrations of  $\text{Li}^7$  and  $\text{B}^{10}$ , the  $\text{B}^{10}$  band nearly disappears and three new bands are observed at 681, 584, and  $522\text{ cm}^{-1}$ . The frequency of the 681- and  $584\text{-cm}^{-1}$  bands depends primarily upon the B isotope, while the  $522\text{-cm}^{-1}$  band depends only upon the Li isotope. The strengths of all three bands are proportional to the B concentration. These results have been interpreted as additional evidence for Li-B ion pairing as originally proposed by Reiss, Fuller, and Morin.<sup>5</sup> If this interpretation of the spectra is correct, then it is expected that the strength of the  $644\text{-cm}^{-1}$  band would increase with increasing temperature while the pair bands would show a related decrease. This expectation is based on the effect of the dissociation of the pairs on the concentration of the species and does not take into account any explicit temperature dependence of the oscillator strengths for the bands.

Several samples of B-doped Si compensated with Li were measured as a function of temperature between room temperature and  $\sim 200^\circ\text{C}$ . The method of compensation has been described previously.<sup>4</sup> Data for a  $\text{B}^{10}\text{-Li}^7$  sample are given in Fig. 1. The points shown were calculated from continuous traces of transmission versus frequency. The total B concentration is  $\sim 2.8 \times 10^{19}\text{ cm}^{-3}$ . The broad absorption band between 630 and  $595\text{ cm}^{-1}$  is a lattice band present in undoped silicon and will not concern us here. In the  $25^\circ\text{C}$  curve the weak  $\text{B}^{10}$  band near  $644\text{ cm}^{-1}$  is seen along with the three strong bands previously described. Weak bands near 655 and  $564\text{ cm}^{-1}$  are due to a small residual  $\text{Li-B}^{11}$  concentration. The anticipated changes in the bands are clearly observed in Fig. 1. A

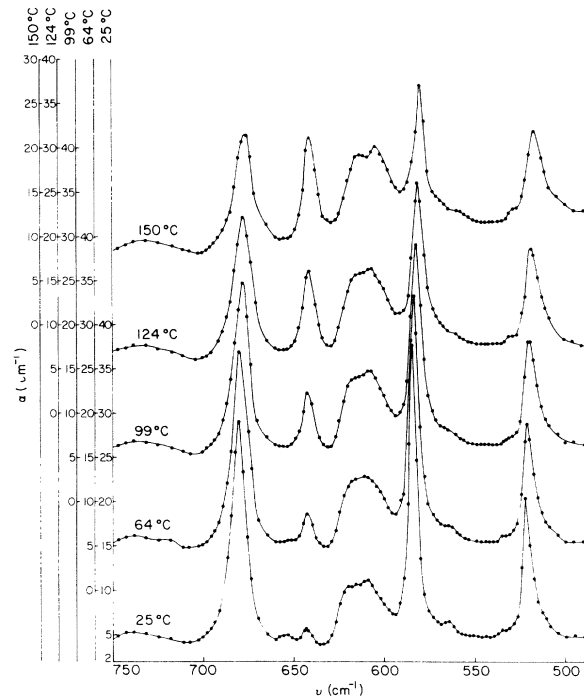


FIG. 1. Absorption coefficient versus wave number for a boron-lithium compensated silicon sample at different temperatures. The boron and lithium concentrations are  $\sim 2.8 \times 10^{19}\text{ cm}^{-3}$ . Note the shifted vertical scales.

gradually decreasing transmission with time at elevated temperatures limits the upper measurement temperature. This decrease of transmission is probably due to precipitation or out diffusion of Li, with a resulting free-carrier absorption arising from holes from uncompensated B.

If the peak absorption coefficient, less background, of the  $681\text{-cm}^{-1}$   $\text{B}^{10}\text{-Li}$  pair band is plotted versus that of the  $644\text{-cm}^{-1}$  B band, the points are found to lie close to a straight line given by  $\alpha_{644} = 19.8 - 0.733\alpha_{681}$ . The peak absorption values were used as there was very little change of width of these two bands in the temperature range studied. The observed linearity is also to be expected.

The peak absorption coefficient of the band at  $584\text{ cm}^{-1}$ , also attributed to  $\text{B}^{10}\text{-Li}$  pairs, shows a decrease with increasing temperature as expected. The peak absorption coefficient is approximately proportional to that of the  $681\text{-cm}^{-1}$  peak; however, as can be seen from Fig. 1, the background absorption near the  $584\text{-cm}^{-1}$  peak is less certain. The concentration  $[\text{B}]$  of unpaired boron, in terms of site fraction, may be determined from the peak absorption coefficient of the  $644\text{-cm}^{-1}$  B band and the known total concentration of B, from  $[\text{B}] = [(\alpha_{644})/19.8] \times (2.8 \times 10^{19}/5 \times 10^{22})$ . The concentration of pairs  $[\text{B-Li}]$  is similarly given, except  $\alpha_{644}$  is replaced by  $19.8 - \alpha_{644}$ .

Application of the mass-action law to the present case gives

$$\frac{[\text{B-Li}]}{[\text{B}][\text{Li}]} = k = A \exp(E/kT).$$

The  $[\text{B}]$  and  $[\text{Li}]$  are equal and each proportional to the  $644\text{-cm}^{-1}$  band-absorption coefficient. The results are shown in Fig. 2, where the experimental equilibrium constant is plotted against  $1/kT$ . The slope gives  $E = 0.39\text{ eV}$  for

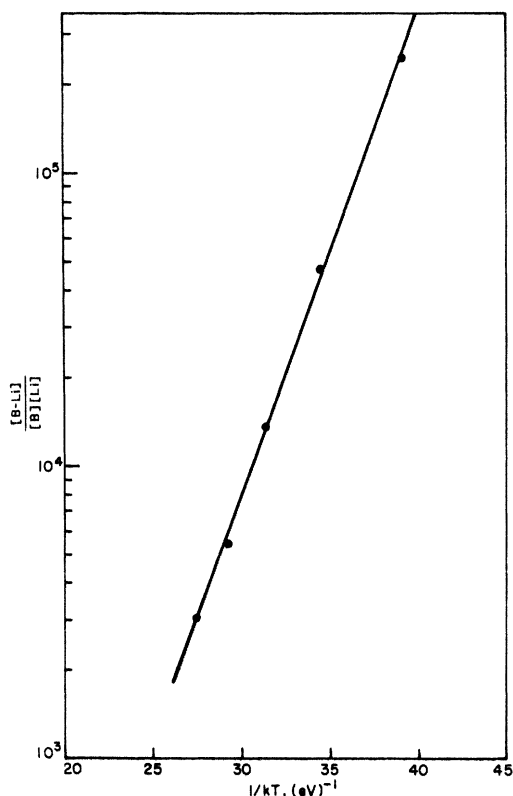


FIG. 2.  $[\text{B-Li}]/[\text{B}][\text{Li}]$  versus  $1/kT$ .

the pairing energy of the  $\text{B-Li}$  pairs. Since the sample is within the range where, at room temperature, the pair bands are directly proportional to the B concentration, the pairing energy should not be seriously modified by interactions between pairs. The present results do not, however, demonstrate whether the simple mass-action relation is maintained at the high impurity concentrations used here. The value of  $E = 0.39\text{ eV}$  is in good agreement with the  $0.39$  to  $0.43\text{ eV}$  obtained by Kroger<sup>6</sup> from an analysis of the Li-diffusion data of Pell.<sup>7</sup> As discussed by Kroger, the simple Coulomb model with this pairing energy predicts a distance of closest approach of  $\sim 2.6\text{ \AA}$  for the Li and B, which is close to the value obtained by Reiss's method.<sup>7</sup>

Similar results were obtained from absorption studies of a  $\text{B}^{10}\text{-Li}^6$  sample, where  $E = 0.36$  to  $0.38\text{ eV}$ . Samples doped with  $\text{B}^{11}$  have the B band at  $620\text{ cm}^{-1}$ , superimposed on the Si lattice band, and hence quantitative measurements are more difficult. However, the qualitative features are the same as those reported here.

The pre-exponential term  $A$ , when the concentrations are expressed as site fractions, is  $\sim 0.1$ . According to theory<sup>8</sup>  $A = Zf$ , where  $Z$  is the number of equivalent nearest sites for Li around the B, and  $f$  arises from the vibrational part of the entropy variation. Although precise values for  $Z$  and  $f$  are not known in the present case, the value  $A \sim 0.1$  is substantially smaller than the values suggested by the Li-diffusion work.

The authors have been fortunate to have a number of interesting discussions with F. A. Kroger and H. Reiss.

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<sup>6</sup>F. A. Kroger, Chemistry of Imperfect Crystals (North-Holland Publishing Company, Amsterdam, 1964), Chap. 9, Sec. 2.

<sup>7</sup>E. M. Pell, J. Appl. Phys. **31**, 1675 (1960).