Dependence of the Excitation Energies of Boron in Diamond on Isotopic Mass

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Abstract

Kim et al. have reported a dependence of the infrared excitation energies of boron acceptors in diamond on the isotopic mass of the carbon atoms. We show that this change can be quantitatively interpreted as induced by a change in the hole effective mass.

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1 Introduction

Kim et al. have investigated the dependence of the infrared excitation spectrum of substitutional boron acceptors in diamond on the isotopic mass of diamond (\(M_i \approx 12\) for a natural diamond, \(M_i \approx 13\) for a synthetic diamond grown out of \(^{13}\text{C}\)) [1]. Six absorption peaks with average energy equal to 351 meV were observed (see peaks 12a,13,14,15,20 and 22 in Fig. 3 of [1]; peak 11 is very weak and will not be included in our considerations). They discovered an increase of 1.26 meV in the average energy of these peaks when replacing \(^{12}\text{C}\) by \(^{13}\text{C}\). They examined various possible origins for this change (e.g., change of the dielectric constant with \(M_i\) [2], changes of a self-energy related to electron-phonon interaction [3]) but were not able to give any convincing explanation for the origin of that dependence on \(M_i\). In this work, we attribute the change in excitation energy to a change in the binding energy of the acceptor related to a change in the hole effective mass. The latter results from the renormalization of the \(E'_0\) gap of diamond by electron-phonon interaction [4]. The \(E'_0\) gap determines, via \(k.p\) perturbation theory, the average hole mass which defines the acceptor binding energy.

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2 Theory

The average excitation energy under consideration (351 meV) is quite close to the ionization energy of the boron acceptor (370 meV) \[5\]. We shall therefore assume that the measured relative change in average excitation energy, \( \Delta E_{ex} / E_{ex} = +3.6 \times 10^{-3} \) \[\Delta E_{ex} = E_{ex}(^{13}\text{C}) - E_{ex}(^{12}\text{C})\], is equal to the corresponding change in binding energy. For nondegenerate band extrema the binding energy of a hydrogenic impurity is:

\[
E_B = 13.6 \frac{m^*}{\epsilon_0} \text{ (eV)},
\]

where \(m^*\) is the effective mass (in units of the free electron mass) and \(\epsilon_0 \simeq 5.7\) for diamond. For electrons in conventional semiconductors, \(m^*\) is, to a good approximation, proportional to an interband gap \[3\]. For holes, however, the relevant bands are degenerate at \(k = 0\) and the acceptor binding energy is determined by the so-called Luttinger parameters, labeled \(\gamma_1, \gamma_2\) and \(\gamma_3\) (see \[6\], p. 174). These parameters are not well known for diamond. We use here the theoretical values \(\gamma_1 = 2.54, \gamma_2 \simeq 0, \gamma_3 = 0.63\) reported in \[7\]. The dominance of \(\gamma_1\) enables us to use for \(E_B\) the “one spherical band” approximation \(\text{(6), p. 176)}\) and to write:

\[
E_B = \frac{13.6}{\gamma_1 \epsilon_0} \text{ (eV)}.\]

It is easy to see, using the data of \[2\], that the dependence of \(\epsilon_0\) on \(M\) is an order of magnitude too small to account for the observed dependence of \(E_{ex}(\simeq E_B)\). Let us therefore consider the dependence of \(\gamma_1\) on \(M\). For this purpose, we use the expression \[4\]:

\[
\gamma_1 = -\frac{4M}{3} \left(2F + 4G + 4M\right) - 1
\]

which for the definition and values of \(F, G,\) and \(M\) given in \[4\] can be written as:

\[
\gamma_1 \simeq -\frac{4M}{3} = \frac{Q^2}{E_0'},\]

where \(E_0'\) represents the lowest direct gap of diamond and \(Q\) the matrix element of linear momentum connecting the valence and conduction states which define \(E_0'\). This matrix element is closely related to \(2\pi/a_0\), where \(a_0\) is the lattice parameter which also depends only weakly on \(M\) \[8\]. We thus assume, as is often done in the spirit of \(k.p\) theory, that the dependence of \(\gamma_1\) on \(M\) results from the corresponding dependence of the \(E_0'\) gap.

3 Results and Discussion

Combining Eqs. (2) and (4) we obtain:

\[
\frac{\Delta E_{ex}}{E_{ex}} \simeq \frac{\Delta E_B}{E_B} = \frac{\Delta E_0'}{E_0'}
\]

Fortunately, a calculated value of the zero-point renormalization of the \(E_0'\) gap of diamond by the electron-phonon interaction has been reported in \[4\]. No experimental data are available for the \(E_0'\) gap of diamond, but data for its indirect gap and various gaps of other semiconductors support the theoretical predictions \[4\]. From the zero-point renormalization \((\simeq -665 \text{ meV for diamond})\) and its expected proportionality to \(M^{-1/2}\) \[109\], we find for \(\Delta E_0' = E_0'(^{13}\text{C}) - E_0'(^{12}\text{C})\):
\[ \Delta E'_0 = \frac{1}{2} \times \frac{1}{12.5} \times 665 \text{ meV} = 27 \text{ meV}. \]  

(6)

Replacing this value of \( \Delta E'_0 \) and \( E'_0 = 7.2 \text{ eV} \) in Eq. (4) we obtain:

\[ \frac{\Delta E_{ex}}{E_x} \simeq \frac{27 \times 10^{-3}}{7.2} = 3.7 \times 10^{-3}, \]

(7)
in excellent agreement with the measurements reported in \([1]\) (3.6 \times 10^{-3}).

4 Conclusions

We have identified the mechanism responsible for the isotope effect on the excitation and binding energy of acceptors in diamond as being due to the renormalization of the \( E'_0 \) gap by the electron-phonon interaction, which is particularly large in the case of diamond.

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