Effect of nitrogen impurity on the structural, mechanical and phonon properties of diamond from first-principle study

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Using a density functional approximation we investigated the structural, mechanical and phonon properties of the diamond doped with nitrogen and compared them with the properties of pure diamond. The calculated results for the pure diamond are in good agreement with experimental data and other ab-initio calculations.

First-principles calculations were performed in the plane wave basis approximation, using the ABINIT package. The pseudopotentials with GGA exchange-correlation functional were used in the structural and elastic calculations and LDA pseudopotentials in the Raman and IR calculations. The structure of the nitrogen-doped diamond was represented by 64-atom cubic supercell (the 2x2x2 repetition of 8-atom elementary diamond cell, where one carbon atom was replaced by nitrogen (NC_{63} cell)) that was relaxed with respect to the atom positions and lattice constants. For the calculating of elastic constants we used the method of small strains imposed to the equilibrium structure. For the computation of phonon density of states we used the direct method of calculating interatomic force constants. The Raman and IR intensities were calculated using the QUANTUM ESPRESSO package.

After the relaxation the lattice constant of nitrogen-doped diamond slightly increases, the elastic constants and moduli reduces. From the radial and bond angle distributions we can conclude that the substitutional nitrogen atom in diamond brought only local distortions in the diamond lattice. In nitrogen-doped diamond the elastic anisotropy decreases, the crystal becomes less brittle. The investigation of elastic anisotropy has shown that isotropic approximation is nonsufficient for the study of elastic properties in both pure and nitrogen-doped diamond. The hardness of nitrogen-doped diamond decreases. The calculated hardness anisotropy of diamond confirmed the experimental data that the hardness of the face (111) is much higher than the hardness of the face (100). The nitrogen doping tends to reduce the hardness anisotropy.

The phonon DOS bands of diamond are shifted down at nitrogen doping that testifies to weakening of interatomic interaction in nitrogen-doped diamond. The study of partial PDOS has shown that the nitrogen contribution is seen only within the PDOS of pure diamond that causes an appearance of resonant localized modes. The modes with the greatest nitrogen participation are more localized in comparison with the majority modes. The maximum at 1220 cm^{-1} in PDOS is due to the carbon atoms contribution, but the carbon atom, which is removed from the nitrogen atom and has three short bonds with nearest carbon atoms, forms the band at 1329 cm^{-1}.Unlike pure diamond the Raman tensor component α_{zz} is not equal to zero. The crossed component α_{xz}, as expected, is largest for modes near 1329 cm^{-1}.

Our calculations are consistent with the following experimental data: a C_{3v} local symmetry of nitrogen site in diamond, a lattice expansion in nitrogen-doped diamond, the frequencies of localized modes of carbons near nitrogen have the highest value in comparison to other modes, the noticeable contribution of nitrogen in IR intensity near 1100 cm^{-1}, the calculated elastic constants in diamond, hardness of the (111) face in diamond is higher than that of the (100) face.

Results of the carried-out calculations showed that, as masses of nitrogen and carbon differ a little, local modes of nitrogen have a resonant character, they are strongly hybridized with the diamond modes and they become poorly localized. On the other hand, a lattice distortion by nitrogen has the local character in nitrogen-doped diamond.