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Raman spectroscopic features of the neutral vacancy in diamond from *ab initio* quantum-mechanical calculations

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Quantum-mechanical *ab initio* calculations are performed to elucidate the vibrational spectroscopic features of a common irradiation-induced defect in diamond, *i.e.* the neutral vacancy. Raman spectra are computed analytically through a Coupled-Perturbed-Hartree–Fock/Kohn–Sham approach as a function of both different defect spin states and defect concentration. The experimental Raman features of defective diamond located in the 400–1300 cm^{-1} spectral range, *i.e.* below the first-order line of pristine diamond at 1332 cm^{-1}, are well reproduced, thus corroborating the picture according to which, at low damage densities, this spectral region is mostly affected by non-graphitic sp^3 defects. No peaks above 1332 cm^{-1} are found, thus ruling out previous tentative assignments of different spectral features (at 1450 and 1490 cm^{-1}) to the neutral vacancy. The perturbation introduced by the vacancy to the thermal nuclear motion of carbon atoms in the defective lattice is discussed in terms of atomic anisotropic displacement parameters (ADPs), computed from converged lattice dynamics calculations.

1 Introduction

Since many years, the investigation of native and radiation-induced point-defects in semiconductors has attracted an ever-increasing interest in both theoretical and experimental studies. This is particularly true in the case of diamond, a wide-bandgap material characterized by well-known extreme physical properties (high Young's and bulk modulus, broad transparency range, high thermal conductivity and carriers mobility, *etc.*) with attractive applications in different fields, ranging from microelectro-mechanical systems to heatsinks, laser windows, particle detectors, *etc.*[1,2] Indeed, the presence of defects in the crystal structure of diamond has a dramatic effect on its physical properties, from structural,[3] optical,[4] and electronic[5] points of view. A rigorous understanding of the physical effects of different typologies of defects is therefore of paramount importance in diamond science and technology.

Despite the large number of studies on the subject,[6–11] the defect formation mechanisms in diamond are still far from having been exhaustively explored and understood. This is especially due to the peculiar meta-stability of its crystalline structure, in which both sp^3 and graphitic-like sp^2 chemical bonds give rise to an unusual variety of different point-defects and related complexes. In this respect, Raman spectroscopy is the ideal experimental technique to study different carbon allotropes due to their characteristic vibrational features,[12,13] and it has thus emerged as a prominent technique to investigate defect formation in irradiated diamond.[6,7,11,14–21]

The Raman spectrum of pristine diamond consists of a single, sharp Raman peak at 1332 cm^{-1}, corresponding to the first-order scattering with triply-degenerated TO(X) phonons of F_{2g} symmetry. The damaged crystal, in contrast, is characterized by several additional features, which have been attributed to different types of sp^2 and sp^3 defects. The most prominent features observed at higher Raman frequencies with respect to the first-order line are located at about 1450, 1490, 1630 and 1680 cm^{-1}. The 1630 and 1680 cm^{-1} features are commonly attributed to sp^2 defects such as the "dumb-bell" split-interstitial defect.[6,16] On the other hand, different tentative attributions have been formulated for the 1450 and 1490 cm^{-1} peaks, involving both vacancy[16,20] and intrinsic/nitrogen interstitial defects.[22,23] At lower Raman frequencies, two broad bands are measured in defective diamond, in the 400–1000 cm^{-1} and 1000–1300 cm^{-1} ranges, respectively.[14,15,17] These vibrational bands are rather articulated and their attribution is unclear.[24] As these broad bands qualitatively resemble the vibrational density-of-states of pristine diamond,[25] they are tentatively

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