Acoustic and optical phonons in metallic diamond

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Abstract

The dispersion of acoustic and optical phonons in highly boron-doped diamond has been measured by inelastic X-ray scattering at an energy resolution of 6.4 meV. The sample is doped in the metallic regime and shows superconductivity below 4.2 K (midpoint). The data are compared to pure and nitrogen-doped diamond that represent the non-metallic state. No difference is found for the acoustic phonons in the three samples, while the optical phonons show a shift of the dispersion (softening) in qualitative agreement with earlier results from Raman spectroscopy. The presence of boron and nitrogen incorporated into the diamond lattice leads to structural disorder. Evidence for this is found both in the observation of otherwise symmetry-forbidden Bragg intensity at (0 0 2) and intensity from acoustic phonon modes in the vicinity of (0 0 2).

Keywords: Hole-doped diamond; Superconductivity; Phonon; Lattice dynamics; Electron–phonon coupling

1. Introduction

Superconductivity in boron-doped diamond is observed at doping levels beyond $n \approx 1 \times 10^{21}$ cm$^{-3}$. The first observation of superconductivity was made in samples grown by high-temperature-high-pressure synthesis [1], which was quickly confirmed in samples grown homo- and heteropitaxially by microwave plasma-assisted chemical vapour deposition ($\mu$-wave CVD) [2,3]. Superconductivity occurs in samples far above the metal-to-insulator transition (MIT) at $n = 3 \times 10^{20}$ cm$^{-3}$ [4]. A small but clearly metallic density of free holes is thus present in the material. Raman spectroscopy provides evidence of a coupling of the holes to the zone-centre optical phonons [5]. In this proceedings report we present data of all acoustic and optical phonon branches in highly boron-doped, pure and nitrogen-doped diamond and discuss the influence of the metallic state on the phonon dispersions. For this experiment a unique thick heteroepitaxial layer of B-doped diamond with a superconducting transition at $T_c = 4.2$ K (midpoint of the resistivity step) was manufactured by $\mu$-wave CVD.

The lattice dynamics of diamond above the MIT is influenced by the presence of free charge carriers that modify the phase space of electron–phonon scattering and by the change of bonding due to the re-distribution of charge. The electronic structure of diamond above the MIT has already been investigated experimentally both by optical spectroscopy [6] and photoelectron spectroscopy [7]. Optical spectroscopy gives evidence for an impurity state-induced band above the valence band edge while the photoelectron spectra show a shift of the Fermi level into the diamond valence band in the fashion of a rigid band shift. The coupling of the free holes has so far only been studied theoretically since the Raman experiments do not allow for a quantitative extraction of the electron–phonon coupling parameters [5].
Density functional theory calculations in the virtual crystal approximation could relate the superconductivity in hole-doped diamond to the high $T_c$ in MgB$_2$ [8–10]. While in MgB$_2$ the metallic bands are two-dimensional and couple to two bond-stretching optical phonon modes, they are three-dimensional in diamond and couple to the three bond-stretching zone-centre optical modes. Supercell calculations that place the boron atoms into specific substitutional sites in the diamond lattice find a similar electron–phonon coupling [11,12]. As a consequence of the electron–phonon coupling, the calculations predict a softening of the affected phonon modes, in particular the optical phonons. While the calculations focus on the coupling to the zone-centre bond-stretching optical modes, details of the dispersion throughout the Brillouin zone have been extracted both from the virtual crystal approximation [8] and from supercell calculations [12]. A strong softening of the optical phonons is predicted throughout momentum space while the acoustic phonons are not softened. The strongest softening is found in the vicinity of the $\Gamma$-point. The acoustic phonons do not contribute to the electron–phonon coupling and are found practically unaffected by the doping in the calculations.

The coupling of the metallic free carriers into Cooper pairs in a superconductor cannot be observed directly. If the coupling mechanism is mediated through some species of quasiparticles, the coupling of the electrons to these quasiparticles can be studied. A very successful probe for this is the observation of dispersion anomalies and peak widths in ultraviolet angle resolved photoemission spectra [13,14]. This probe is however not specific to the kind of quasiparticles since the electron's spectral function will show similar features for all kinds of bosonic excitations. The observation of the phonon dispersion and lifetimes on the other hand provides a complementary view of the electron–phonon coupling that is specific even to the quasiparticles since the electron's spectral function will show similar features for all kinds of bosonic excitations. The observation of the phonon dispersion and lifetimes on the other hand provides a complementary view of the electron–phonon coupling that is specific even to the quasiparticles since the electron's spectral function will show similar features for all kinds of bosonic excitations.

The diamond lattice consists of tetragonally coordinated $sp^3$ hybridized carbon atoms with very short covalent bonds. The extreme hardness and brittleness of the material and also the high Debye temperature $T_D = 2200\,\text{K}$ are macroscopic consequences of the strong covalent bonding. The crystal structure has a two atomic basis, thus six distinct phonon branches can be observed. We distinguish the steeply dispersing acoustic modes (A) and the optical modes (O) of very high frequency (164 meV at the $\Gamma$-point due to the strong and stiff bonds). At $\Gamma$ all optical modes are degenerate. Along the high-symmetry directions of the crystal the degeneracy is partially retained and the dispersion splits into transverse (TA and TO) and longitudinal (LA and LO) phonon branches. Diamond was one of the first materials to be investigated with the technique of inelastic neutron scattering (INS) [16], although the high frequencies of the optical mode impose a difficulty when thermal neutrons are used. Even such fine details as the over-bending of the LO branch have been studied in detail both by inelastic neutron and more recently by X-ray scattering techniques [17].

In this paper the technique of inelastic X-ray scattering (IXS) is employed. Similar to INS, energy loss spectra of X-rays are measured in a scattering geometry where the momentum transfer to the crystal system is given by the scattering of the photon. The use of IXS has several advantages over INS for the investigation of the phonon dispersions of B-doped diamond. While the first neutron scattering experiments on diamond were performed on large jewels borrowed from the Smithsonian Institution museum [16], the small beam diameter of $\approx 100\,\mu\text{m}$ in IXS allows for a much smaller sample volume. The small absorption of the X-rays by the light elements makes the whole cylindrical volume through the sample along the beam available for the experiment. In the case of neutrons the absorption by $^{10}\text{B}$ would be quite severe and isotope enriched samples of $^{11}\text{B}$ should be used. Large energy transfers as for the optical phonons in diamond are no difficulty in an IXS experiment in contrast to thermal neutrons.

2. Samples and experiment

A sample of highly B-doped diamond was grown by epitaxial growth using microwave plasma-assisted CVD on an existing heteroepitaxial diamond film on Si(0 0 1) with a SiC buffer layer [18] (sample B). The silicon was etched away prior to the IXS experiment to avoid a background signal from the substrate (see Fig. 1a and b). CVD growth was carried out during 106 h in 10 sessions to achieve a final sample thickness of $\approx 100\,\mu\text{m}$. The vacuum system of the growth apparatus had to be interrupted once during the growth to restore the microwave system that got covered by conducting metallic diamond. Deposition was carried out at 50 Torr pressure at 900 °C with a diluted gas mixture of methane and trimethylboron (TMH) in hydrogen. The methane concentration was 3% and the B/C ratio 2000 ppm. The B concentration in the sample was determined by secondary ion mass spectroscopy (SIMS) as $n = 3.8 \times 10^{21}\text{cm}^{-3}$ (2.5 at%). The highly doped character of this sample is evident from the dark grey colour and the metallic lustre. The almost flat temperature-dependent resistivity curve shows a superconducting transition with an onset at 6.4 K as shown in Fig. 1c.

A second sample of nitrogen-doped CVD diamond was grown by the same technique earlier [18] (sample N). This sample had accidentally peeled off the Si(0 0 1) substrate during the cooling at the end of the deposition and a free standing film of N-doped diamond was obtained (Fig. 1b). This sample served as a reference for non-metallic diamond. The N-doping level of this sample is of order...
ppm, thus insulating properties are retained leading to a yellowish transparent sample. Since nitrogen forms a deep donor level in diamond, the N-doped samples remain insulating at room temperature and below up to very high doping levels. From the point of view of electron–phonon coupling and lattice expansion, sample N was found to be equivalent to pure diamond.

Both samples were characterized by conventional X-ray diffraction (XRD) using Mo K$_\alpha$ radiation at $\lambda = 0.709$ Å. To achieve a good definition of the momentum transfer $Q$ in the IXS experiment a low mosaic spread is required. The samples have a smooth distribution of crystallite orientations as shown in Fig. 1d with a width of $<0.7^\circ$ (FWHM) for sample B and $<1.3^\circ$ for sample N. The symmetry of the diamond lattice does not allow diffraction of the (002) Bragg reflection, which is not observed in pure diamond. In the doped samples the reflection could become allowed due to the difference in atomic form factor $f_0$ for C and B and for C and N, respectively. In sample B the (002) reflection was observed about 200 times weaker than the principal reflection (004). In sample N it was only barely visible, 1000 times weaker than the (004) reflection. Since the difference of the atomic form factor is similar both for B vs. C and for N vs. C, these intensities directly reflect the incorporation of B and N atoms into the lattice. The observation of a (002) reflection shows that incorporation of the B and N atoms is not completely random and the symmetry of the diamond lattice is changed. Impurity–impurity interaction leads to some ordering in the B or N subsystem. Doping with boron also leads to a slight expansion of the lattice, which was observed in the XRD experiments, while the N-doping leads to no or negligible lattice expansion.

The IXS experiment was performed at the IXS station at beamline 35XU at the SPring-8 synchrotron radiation light source [19]. The energy resolution was set to 6.4 meV by use of the Si(8 8 8) reflection in the backscattering monochromator and in the diced spherically bent analysers with a photon energy $h\nu = 15.82$ keV. Detuning of the incident monochromator with respect to the analyser crystals is done by ramping the temperature of the monochromator. Of the 12 analysers available we focussed on the four in the scattering plane as they provide information along the common high-symmetry direction for longitudinal modes. A scan over the full range of energy loss from −30 to 180 meV took about 7 h. The energy scale was calibrated for each analyser using the elastic line position and the optical phonon peak from a pure single crystal diamond sample close to the Γ-point at $\mathbf{Q} = (1.1, 1.1, 1.1)$ [17].

The choice of the scattering geometry allows the observation of specific phonon modes. If the reduced phonon momentum $\mathbf{q} = \mathbf{Q} - \mathbf{G}$ and the total momentum transfer $\mathbf{Q}$ are aligned, only longitudinal phonons can be observed. $\mathbf{G}$ represents the position of the nearest Γ-point. Transverse phonons are observed when $\mathbf{q}$ and $\mathbf{Q}$ are at an angle. Spectra have been acquired in a longitudinal geometry with $\mathbf{Q} = (1.07, 1.07, 1.07)$ to $\mathbf{Q} = (1.53, 1.53, 1.53)$ for the [1 1 1]-direction Γ–L and $\mathbf{Q} = (0 0 2.06)$ to $\mathbf{Q} = (0 0 3.05)$ for the [0 0 1]-direction Γ–X and an additional mostly transverse spectrum at the L-point, $\mathbf{Q} = (0.5, 1.5, 0.5)$. All experiments were performed at room temperature and with the sample in air.
3. Results of IXS

The spectra of IXS are shown in Fig. 2. The steep dispersion of the LA and the slight dispersion of the LO phonons in the [1 1 1]-direction can be traced from the raw data in Fig. 2a. The lowest four spectra close to the (1 1 1) Γ-point have been acquired for samples B and a single crystal of pure diamond. While pure diamond shows no elastic intensity off the Bragg point, sample B has a strong elastic peak that prevents data acquisition closer to (1 1 1).

Fig. 2. (a) IXS spectra along the [1 1 1]-direction from close to the zone centre (bottom) to the zone boundary at L (top) and (b) along the [0 0 1]-direction from the zone centre (bottom) to the zone boundary at X (top). The data are stacked according to momentum transfer. The spectra are measured in a longitudinal IXS geometry, except for the topmost spectrum in (a) at the L point for transverse phonons. Data from the B-doped sample B are shown as squares with statistical error bars, data from pure diamond and sample B as solid lines.
The spectra of these two samples show matching peak positions for the acoustic phonons LA and the same trend of intensity as a function of momentum transfer. The peak widths are limited by the resolution of 6.4 meV. The peak positions of the optical phonons LO in pure diamond [17] and sample N agree within the uncertainty of the energy calibration. The optical phonon peaks LO of sample B are shifted to lower energy and broadened. This broadening is severe close to the zone centre and reduced at the zone boundary. The transverse phonons show the same behaviour as the longitudinal phonons at the zone boundary point L, the acoustical phonon TA is unchanged and the optical phonon TO shows a shift and a slight broadening.

The spectra along Γ–X shown in Fig. 2b show the same behaviour. Samples B and N have a strong elastic peak, especially close to the Γ-point (002) at the bottom of the figure. The pure diamond sample on the other hand gives only a tiny elastic peak exactly at (002). The scaling of the overall intensity in Fig. 2b was chosen such that the optical phonon peaks LO overlap in the stacked spectra. The weak features of dispersing acoustic phonons LA and TA thus become visible in the intermediate energy transfer region in sample B. The dispersion of feature TA from zero energy at the Γ-point and the backfolding at the zone boundary are seen clearly. The LA phonon gives only a weak feature that disperses into a degeneracy with the LO phonon at the zone boundary. Its dispersion can be traced clearly in sample B but also sample N shows this feature as a small shoulder of the LO peak in the fourth spectra from the top of Fig. 2b. The pure diamond sample shows vanishing intensity from the acoustic phonons in agreement with model calculations.

4. Discussion

A compilation of all peak positions extracted from the data is shown in the dispersion plot in Fig. 3. The acoustic phonon dispersions fall on top of each other for samples N and B within the error limits. The speed of sound is thus unchanged in the presence of the free charge carriers in sample B with respect to pure diamond. In the case of highly doped silicon it was found that the screening due to the free carriers leads to a small but measurable change of the dispersion of acoustic phonons [20]. In our data such tiny changes are not detectable due to the limited energy resolution.

The dispersions of the LO phonons in sample B and N run parallel with a peak shift of 2 meV for a certain range from the zone boundary inward to about half the distance to the Γ-point in both high-symmetry directions. While the dispersion of pure diamond and thus also sample N is almost flat around Γ, the data from sample B show a clear dip. In sample N the over-bending of the LO phonon is around 1 meV along the Γ–X line and less than 0.5 meV.
along the Γ–L line. In sample B the over-bending is strongly increased to more than 5 meV along Γ–X and 3 meV along Γ–L. The detailed analysis of the dispersion suffers however from the uncertainty of the determination of the peak position due to the highly asymmetric peak shape of the optical phonon peaks in sample B. The peak width of the LO peaks also increases towards the Γ-point while it is constant for a certain momentum range to the zone boundary (see Fig. 2). The implications of this momentum dependence of this softening are discussed in a separate publication [21].

The observation of a clear intensity of the acoustic phonons in sample B along the [0 0 1]-direction is in contrast with model calculations that otherwise reproduce the intensities accurately. In the doped samples the (0 0 2) Bragg reflection becomes kinematically allowed as discussed above, while it is symmetry forbidden in pure diamond. As a rule of thumb the intensity of acoustic phonons scales with the static structure factor of nearby Bragg points. Since (0 0 2) has a clear intensity it is not surprising to see the LA phonon in this longitudinal IXS geometry. The TA phonon, however, has no longitudinal character in pure diamond and is not observable in this scattering geometry. Frequencies and dispersion of feature ‘‘TA’’ in the data match the well-known transverse acoustic phonon in pure diamond along [0 0 1] [16]. We thus conclude that the presence of lighter boron atoms introduces some longitudinal character into this mode and thus the assignment as a transverse mode is no longer strictly correct.

In conclusion we have measured the dispersion of acoustic and optical phonons along the [1 1 1] and [0 0 1] high-symmetry lines in pure, nitrogen-doped and highly boron-doped diamond. The dispersion of the acoustic phonons is not influenced by the presence of a metallic state in the boron-doped sample within the error bars. The optical phonons on the other hand show a clear response in accordance with the observation of zone-centre optical phonon softening in Raman spectroscopy. The softening is discussed in a separate publication [21]. In the doped samples B and N, the intensity of the (0 0 2) Bragg spot becomes finite while this reflection is forbidden and not observed in pure diamond. Similarly, acoustic phonon modes become visible close to (0 0 2) along the [0 0 1]-direction. Their dispersion matches the well-known dispersion of the transverse and longitudinal acoustic modes in pure diamond.

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