Phonon Softening in Superconducting Diamond

Superconductivity in highly boron doped diamond has been reported in 2004 [1]. Pure diamond is an insulator with a large band-gap of 5.5 eV. It is a clear, colourless material of extreme hardness, which makes it attractive for jewellery after sophisticated polishing. At low doping, boron forms an acceptor level of 370 meV binding energy, thus the material becomes a hole-doped semiconductor. This electronic level is also responsible for the colour of the famous blue diamond. At very high doping above the metal-to-insulator transition (MIT), at a doping level $n \approx 3 \times 10^{20}$ cm^{-3}, B-doped diamond becomes metallic. The colour changes to a dull grey, but the metallic state makes it interesting for scientific research. Superconductivity was reported above $n \approx 1 \times 10^{21}$ cm^{-3}. The transition temperature T_c depends on the doping level and on the growth conditions. The highest T_c reported so far is a CVD grown sample with a doping of $n = 8.4 \times 10^{21}$ cm^{-3} and an onset of superconductivity at 11.4 K [2].

To understand this rather high superconducting transition temperature at quite low carrier concentrations of less than 0.05 holes per atom two questions have to be addressed: (i) What is the nature of the metallic carriers in B-doped diamond? (ii) How do the holes couple to form Cooper pairs, the key ingredient of the superconducting state? Question (i) has been addressed by optical spectroscopy and by electron spectroscopy [3]. To address question (ii) the coupling of the metallic holes to the lattice vibrations (phonons) of diamond was investigated in this work. This interaction can then account for the coupling in between the holes that is needed to form the superconducting charge carriers.

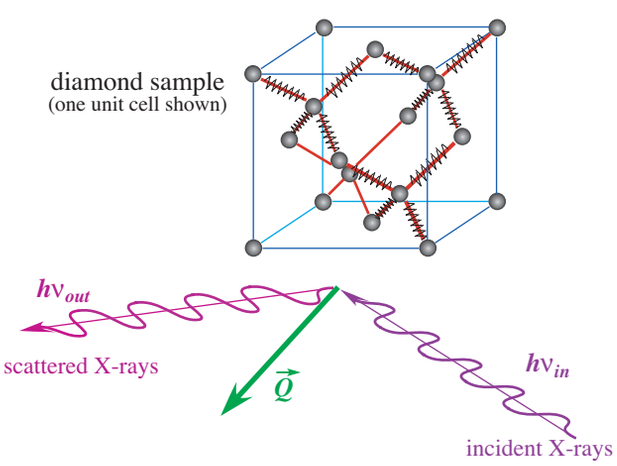

Fig. 1. Schematic view of an IXS experiment. X-rays are scattered with a given momentum transfer Q and excite lattice vibrations in the sample that lead to an energy loss of the X-ray photons.

The hole-hole coupling must be rather strong in the B-doped diamond to lead to such high T_c.

In our experiment we studied the coupling of the metallic charge carriers to the lattice vibrations through the measurement of the dispersion of the phonons. The lattice vibrations are excited when an X-ray photon is scattered in the crystal and looses a small portion of its photon energy according to the frequency of the phonon (see Fig. 1). Measurements at various momentum transfers allow one to trace the dispersion, i.e, the momentum dependence of the phonon frequencies. In diamond, both steeply dispersing acoustic and weakly dispersing optical phonons are present. The frequency of the optical phonon is extremely high (164 meV at the Brillouin zone centre for pure diamond), which reflects the hardness of the material due to the strong short bonds. The experiment was performed at the inelastic X-ray scattering spectrometer (IXS) at beamline **BL35XU**. All measurements were performed at room temperature.

It is difficult to make samples of highly boron doped diamond. In particular single crystals cannot be grown by any standard techniques. In this experiment two samples grown by microwave assisted chemical vapour deposition (CVD) were used. A growth time of over 100 hours leads to a thickness of around 100 μm. The diamond was deposited on a specially prepared silicon substrate with a SiC buffer layer that provides a high degree of epitaxial orientation of the diamond grains. The silicon was etched away to expose only a free-standing diamond layer to the X-ray beam. The samples are shown in Fig. 2(b). A sample of superconducting diamond was grown with a boron concentration of $n = 4.8 \times 10^{21}$ cm^{-3}. It exhibits superconductivity with an onset at 6.4 K as shown in Fig. 2(c). A second sample of nitrogen doped diamond served as a reference for the insulating state and was found to be equivalent to pure diamond for all practical purposes of this experiment. Rocking curves of X-ray diffraction are shown in Fig. 2(d). At a width of around 1° (FWHM) the crystallite orientation is good enough to allow for a well-defined momentum transfer in the experiment.

The presence of metallic charge carriers changes the lattice dynamics and the electron-phonon coupling can shift the phonon frequencies to lower values (softening). The measured dispersion of the phonons along two high symmetry directions of the crystal lattice is shown in Fig. 3. The acoustic phonons show no difference between B-doped metallic diamond and

N-doped insulating diamond. Their dispersion is in good agreement with the well-known results for pure diamond. The optical phonons on the other hand show a strong softening as B-doping is introduced. Close to the zone boundary (X-point and L-point) the softening is constant at about 2 meV over a certain momentum range. Close to the zone centre it becomes stronger with an extrapolated value of ~8 meV at the Γ-point. The softening-curve, i.e. the momentum dependent peak shift between N-doped and B-doped diamond is shown in the top part of Fig. 3.

The observation of strong softening is a clear indication of electron-phonon coupling in diamond. Theoretical predictions (e.g. Ref. [4]) have related this coupling to the superconductivity and found that it can account for the observed transition temperatures. The increased softening close to the zone centre is compatible with the existence of a "spheroid" Fermi surface of the metallic holes as observed in Ref. [3]. For phonon momenta smaller than the diameter of this Fermi surface the coupling is stronger because momentum conserving electronic excitations are possible. For larger momenta the phase space of coupling is reduced and a smaller and constant coupling results.

This result shows that electron-phonon coupling is a good candidate to explain the formation of superconducting hole-hole pairs in a BCS theory.

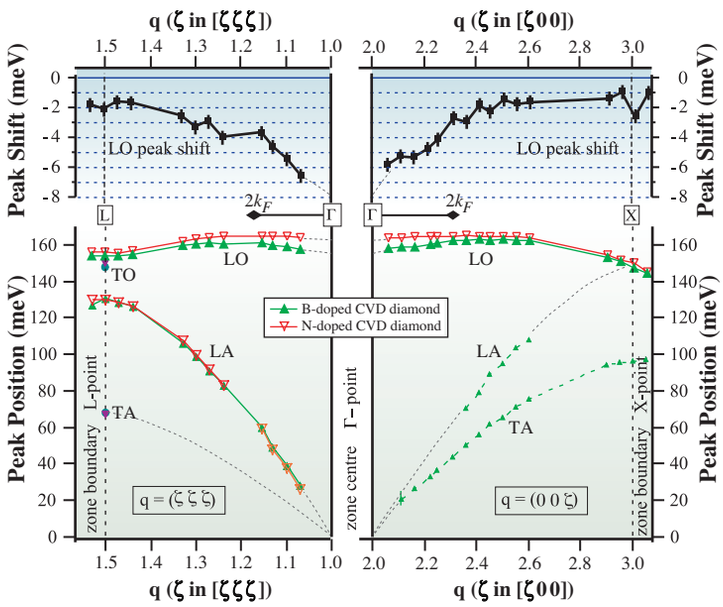

Fig. 3. Measured phonon dispersion in N-doped (open triangles) and B-doped (closed triangles) diamond in two different high-symmetry directions of the diamond lattice. The top part shows the difference of the dispersions of the optical phonons, i.e. the momentum dependent softening. The maximum spanning of the Fermi surface is marked as $2k_F$. It coincides with the range of strong softening. The acoustic phonons are not softened.

Based on the softening, a quantitative estimate of the electron-phonon coupling strength is possible. The extremely high frequency of the optical modes in diamond provides the strong coupling that is needed to form a superconducting state at low carrier concentrations but with remarkably high transition temperatures.

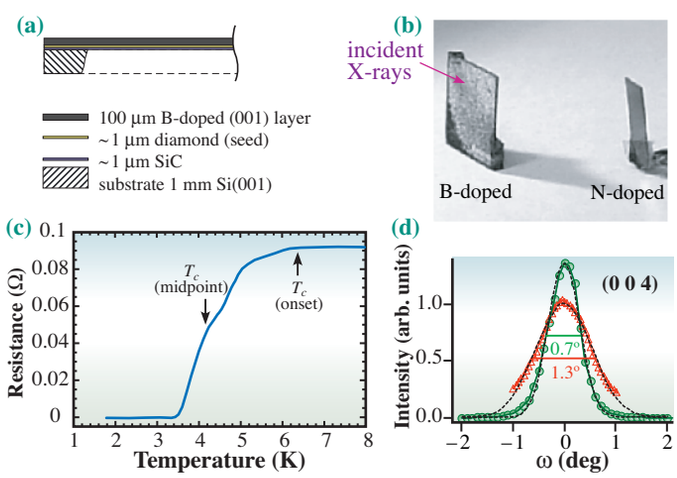

Fig. 2. Samples of CVD grown diamond. **(a)** Schematic view of the B-doped sample. **(b)** Photograph of both the B-doped and the N-doped sample. **(c)** Electrical resistance *vs.* temperature in the region of the superconducting transition in the B-doped sample. **(d)** Rocking curves of X-ray diffraction for the B-doped sample (circles) and the N-doped sample (triangles). The widths of the rocking curves (FWHM) are indicated.

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