Phonon Softening in Superconducting Diamond

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Introduction

Superconduction in highly Boron doped diamond has been reported about two years ago [1] in high pressure-high-temperature grown diamond and confirmed very quickly in CVD grown samples. In the last year a number of publications have appeared and experiments have been performed to understand the rather high transition temperatures with an onset of up to 11 K [2] at very low carrier concentrations of the order of 0.05 carriers per carbon atom. Several theoretical arguments were given in favour of the formation of a metallic band of hole carriers by a rigid band shift, i.e. the location of the Fermi level up to 1.5 eV below the conduction band edge, depending on the number of holes. Experimental evidence for such a Fermi surface of degenerate diamond holes was given by angle-resolved photoemission experiments [3]. In the low doping regime Boron forms an acceptor level at 370 meV binding energy. Another model of metallization considers the overlap of these impurity states to form a Boron induced metallic impurity band. A co-existence of two metallic contributions is possible.

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 diamond lattice has a two-atomic basis on an fcc Bravais lattice. In the high symmetry directions two acoustic (LA and TA) and two optical (LO and TO) modes are observable. The frequency of the optical phonon is extremely high (164 meV at the zone centre for pure diamond), which reflects the hardness of the material due to the strong short bonds. The presence of metallic charge carriers changes the lattice dynamics and the electron-phonon coupling can shift the phonon frequencies to lower values (softening). Theoretical work that predicts this electron-phonon coupling and relates it to the superconductivity reports a shift of the zone centre optical phonon by more than 25 meV at a doing level of 3 at% [4], far more than the softening observed in Raman scattering experiments of less than 4 meV [5]. Small or no softening is predicted for the acoutic phonons.

Experiment

The experiment was performed at room temperature at the inelastic x-ray scattering station of BL35XU at SPring-8. The energy resolution was set to 6.4 meV by use of the Si(888) reflection in the backscattering monochromator and in the diced spherical 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 4 in the scattering plane as providing information along the common high symmetry direction for longitudinal modes. 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 $\vec{Q} = (1.1\ 1.1\ 1.1)$.

Epitaxially grown B-doped diamond was prepared by microwave plasma assisted CVD growth. As previously observed [2], growth of the diamond along the (111) direction leads to higher T_c compared to growth along (001) at the same doping level as determined by secondary ion mass spectroscopy SIMS. For growth along the (111)-direction (sample A)

Boron doped diamond was deposited on a pure diamond buffer layer on a Pt(111) substrate leading to (111) oriented grains with a mosaicity spread of $< 1.5°$. In in-plane orientation of the grains is not well-defined and thus only the dispersion along (111) can be measured with a good momentum definition given by the mosaicity spread. The Pt substrate broke off during sample cooling after deposition leaving a free-standing diamond film of $\approx 100\mu$m thickness. For growth along (001) (sample B) the B-doped material was deposited on an existing 1μm thick heteroepitaxially grown N-doped diamond film on 1μm SiC on Si(001). A total film thickness of $\approx 100\mu$m with a mosaicity of $< 0.8°$ was achieved by 106 hrs. of CVD growth. The Si substrate was etched away after film growth, so that a plate of $\approx 100\mu$m diamond with $\approx 1\mu$m each of N-doped diamond and SiC was exposed to the x-ray beam. The B-content in both films was $\approx 4 \cdot 10^{21}\text{cm}^{-3}$ (2.5 at%). The superconducting transition sets in at $T_c = 7$ K and $T_c = 6.4$ K for samples A and B respective. A third sample of Nitrogen-doped CVD grown diamond of similar thickness was used for reference (sample N).

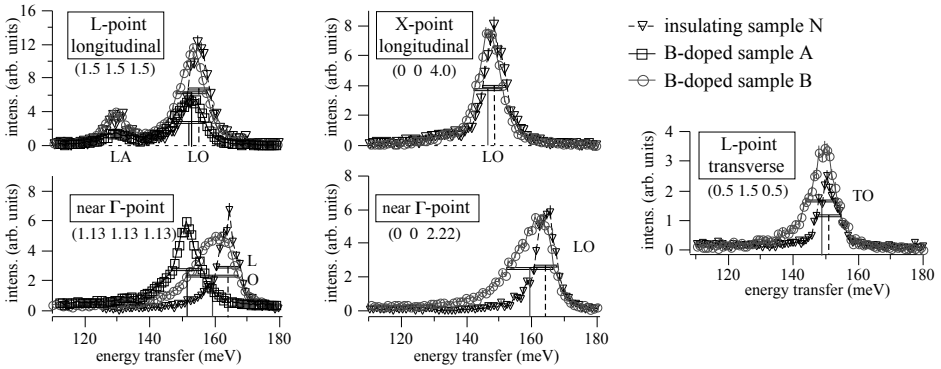

Figure 1: IXS spectra from sample N ($\triangledown$), sample A ($\square$) and sample B ($\circ$) for momentum transfer along the [001] direction (a and b) and the [111] direction (c and d) in a geometry where only longitudinal phonons contribute as well as at $\vec{Q} = (0.5\ 1.5\ 0.5)$ where mostly transverse phonons contribute. The total momentum transfer is indicated for each set of spectra.

Figure 1 shows spectra of inelastic x-ray scattering in the region of the optical phonons for selected points in momentum space. At the zone boundary both in the (111) direction (L-point) and in the (001) direction the B-doped samples A and B show a slight shift of the LO and TO peak positions while the LA peak is unshifted. The optical phonon peaks are slightly broadened with respect to the resolution limited peaks on sample N. Close to the Γ-point the shift of the peaks is strong and the LO peaks from sample B show a very strong and highly asymmetric broadening.

From the spectra the dispersion was extracted by determining the peak position as the centre between the two flanks of the peaks. This yields the dispersion curves shown in the top part of Fig. 2. Sample N shows the well-known dispersion of pure diamond including the slight over-bending of the LO modes, in particular along the (001) direction. In sample B the softened LO dispersion runs parallel to the pure diamond dispersion for a certain momentum range around the zone boundary. Close to the zone centre the softening becomes bigger and a dip of the dispersion around Γ results. In sample A the region of weak softening around the zone centre is small and the softening at Γ is strong resulting in an almost flat dispersion. Fig. 2b) shows the corresponding softening curves, i.e the momentum dependent peak difference between samples N and B and N and A respective. The peak width shown in Fig 2b) is almost resolution limited throughout the Brillouin zone for sample N. In sample B the peak width follows the softening curve and also the asymmetry of the peaks is strong close to the zone centre and small around the zone boundary. Sample A shows a much less pronounced peak-width curve although the peaks are widened beyond the resolution limit throughout momentum space.

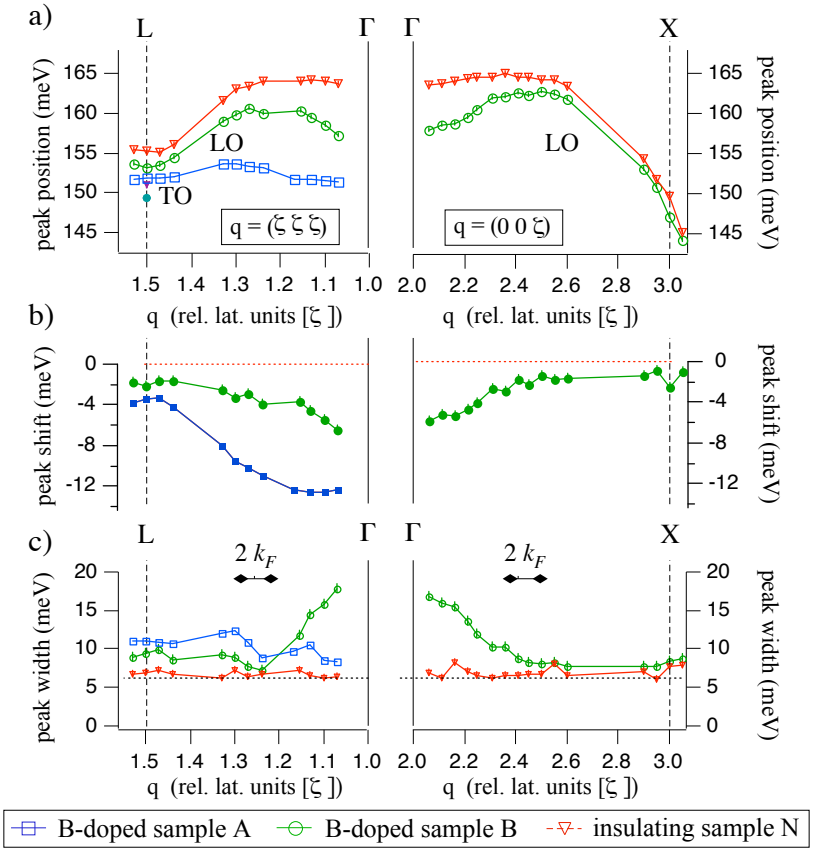

Figure 2: (a) Dispersion of the optical phonons for sample N (▽), sample A (□) and sample B (○) for momentum transfer along the [001] direction (a and b) and the [111] direction (c and d) in a geometry where only longitudinal phonons contribute as well as at $\vec{Q} = (0.5\ 1.5\ 0.5)$ where mostly transverse phonons contribute. (b) Softening curve as discussed in the text. (c) Momentum dependent peak width for the three samples.

Discussion

The softening of the optical phonons shows that strong coupling of the metallic holes to the lattice dynamics of diamond is present in highly Boron doped diamond. The peak shift is larger than the single-phonon peak shift observed in Raman spectroscopy [5]. Due to various effects it is difficult to analyse the Raman spectra in detail but a upper boundary of about 5 meV peak shift can be extracted from those data. On the other hand the peak shift is smaller than the one predicted by theoretical calculations that rely on a perfect, disorder-free single crystal. Effects of the impurity atoms have been observed in our data though the emergence of strong elastic scattering intensity at otherwise symmetry forbidden Bragg points such as (002). In addition a certain macroscopic sample inhomogeniety must be assumed that leads to a rather broad superconducting transition over a temperature range of $\approx$ 3 K with several steps in sample B and a slightly sharper transition over $\approx$ 2 K in sample A (data not shown). This inhomogeniety can also account for the asymmetric and strong peak broadening near the zone centre, where regions of different broadening overlap in the spectra to produce a widened peak..

The characteristic momentum dependence of the softening is compatible with the presence of a "spheroid" Fermi surface, i.e. a single closed Fermi body around Γ. The maximum diameters of such a Fermi surface in different momentum directions is marked in Fig. 2 as $2k_F$. These diameters have been determined from the same kind of *ab initio* calculations

as in [4]. For phonon momenta smaller than the diameter of the Fermi surface all kinds of momentum conserving excitations provide a strong coupling, while the larger momenta that exceed the Fermi surface diameter can couple only indirectly. The two samples A and B show different cut-off momenta for this coupling, thus a difference in the Fermi surface volume can be suspected. A model of metallicity in a Boron related impurity band might also lead to phonon softening but no theoretical predictions are available to test this model against the present data set.

Our data thus support the model of a BCS type superconductivity in Boron doped metallic diamond in analogy to self-doped MgB_2. The measurement of phonon dispersions throughout momentum space offers several advantages over Raman spectroscopy that probes only specific momentum points and suffers from a complicated interaction mechanism. The peak width cannot be attributed directly to the intrisic peak width due to the reduction of phonon lifetime through the electron phonon coupling, but the characteristic momentum dependence is compatible with an electron-phonon coupling within a spheroid Fermi surface. This data set provides a strong test ground for all theories of superconducting in diamond.

We would like to thank the Japan Synchrotron Radiation Research Institute (JASRI) for granting beamtime under project numbers 2004B0736-ND3d-np and 2005A0596-ND3d-np. Dr. Sakaguchi at NIMS characterized the samples by secondary ion mass spectroscopy. One of us (MH) would like to thank the Japanese Society for the Promotion of Science (JSPS) for financial support.

References

[1] E.A. Ekimov *et al.* Nature 428 (2004) 542.

[2] H. Umezawa, T. Takenouchi, Y. Takano, K. Kobayashi, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, G. Zhong, M. Tachiki, H. Kawarada, cond-mat/0503303

[3] T. Yokoya *et al.* Nature 438 (2005) 647.

[4] L. Boeri, J. Kortus, O.K. Andersen, Phys. Rev. Lett. 93 (2004) 237002.

[5] E. Bustarret, E. Gheeraert, K. Watanabe, Phys. Stat. Sol. (a) 199 (2003) 9.