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Effect of nitrogen impurities on the Raman line width in diamonds

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Abstract. The dependence of the Raman line width in diamonds on the nitrogen impurity is experimentally studied. A linear relation between the nitrogen content and the width is found. It is demonstrated that the slope of the linear fit depends on the type of nitrogen defect. A relation between the Raman experiment and results from lattice parameter experiments is found and discussed.

1. Introduction

Diamonds attract the attention of scientific researchers not only due to their technological potential related to unique physical properties. Being one of the simplest of all crystalline solids, diamond serves also as a simple prototypical system for solid state physics. Theoretical models for various physical topics are often tested on this material.

One of the intriguing topics in solid state physics is the effect of impurities on the structural and dynamical properties of an ideal crystal. The overwhelming majority of both natural and synthetic diamonds contains an appreciable amount of nitrogen impurity. It is known that nitrogen in diamond can be in different forms, the dominant being single substitutional N atoms (C centre), pairs of adjacent substitutional N atoms (A centre) and complexes of four substitutional N atoms tetrahedrally sited about a vacancy (B centre). These defects disturb the crystalline lattice and induce infrared absorption in the one-phonon region, which is forbidden in the perfect diamond lattice. Also, the lattice defects create additional channels for the relaxation or scattering of host vibrational modes. An interesting question here is how strong the interaction is between the nitrogen defects and phonons, which results in the phonon attenuation. The effect of different defects on propagation of acoustic phonons has been extensively investigated, e.g., by studying thermal conductivity of diamond (Berman 1979, Bokii *et al* 1986, Ositinskaya *et al* 1993). Much less is known about the influence of nitrogen defects on optical phonons.

The goal of the present work is to study the effect of nitrogen impurities on the attenuation of optical phonons by the Raman light scattering technique. The attenuation of optical phonons leads to broadening of the corresponding line in the Raman scattering spectrum. In the work of Sobolev *et al* (1998) a correlation between the Raman line width and the nitrogen concentration was found in the light scattering experiment on a batch of natural diamonds. Also, in the paper

of Hanzawa *et al* (1996) a small broadening was noted with increasing nitrogen concentration. The results of these works encourage a detailed experimental study of this question. Using well characterized synthetic diamonds, we carefully studied the relation between the nitrogen concentration and the Raman line width. We found a linear correlation between the impurity content and the Raman line width. It is observed that the slope of the line depends on the type of nitrogen defect.

2. Experiment

2.1. Sample preparation and characterization

Synthetic diamond crystals used in the present work were grown by the temperature gradient method using high pressure apparatus of a ‘split sphere’ type (BARS) (Pal’yanov *et al* 1997). Ni–Fe alloy was employed as a solvent catalyst. To vary the concentration of nitrogen impurity in the diamond crystals, additives of nitrogen getters (Ti) and nitrogen-containing compounds (Fe_2N , K_2CN_2 , CaCN_2) were used. Growth runs were performed at a temperature of 1400 °C. Seed crystals were oriented by the (111) plane.

For the purpose of comparing the effect of single substitution and aggregated forms of nitrogen on the Raman scattering spectrum, several diamonds were annealed at 1800 °C for 10 hours under a stabilizing pressure of 6.5 GPa via an apparatus used for diamond synthesis. This treatment resulted in a complete conversion of the C-form nitrogen into the A form.

The form and concentration of nitrogen impurities in our diamond samples were determined from the infrared absorption spectroscopy. Absorption spectra in the defect-induced one-phonon region (1400–900 cm^{-1}) were measured on a Specord-M80 spectrophotometer. The nitrogen content in diamonds was determined from the absorption coefficients at frequencies of 1130 and 1282 cm^{-1} , related to C and A centres, respectively. In order to calculate the nitrogen concentration from the absorption coefficient at these frequencies, we used relationships obtained in the works of Kiflawi *et al* (1994) and Boyd *et al* (1994).

Infrared measurements revealed that the dominant form of nitrogen impurity in the as-grown ungettered diamonds is single substitutional atoms (C centres) with the concentration ranging from about 200 to 800 parts per million. The results of characterization of the diamond samples used are summarized in table 1. A diamond crystal (Q108) grown with addition of 2 wt% of Ti did not show detectable infrared absorption. However, the absorption spectrum measured in the ultraviolet region displayed weak absorption features related to C centres.

Table 1. Synthetic diamond samples and their parameters. N_C and N_A are concentrations of nitrogen in the C and A forms, respectively, γ_L is the Raman line width (FWHM) for the Lorentzian fit, γ the FWHM corresponding to zero spectral slits as found from the Voigt contour description.

Name	N_C (ppm)	N_A (ppm)	γ_L (cm^{-1})	γ (cm^{-1})
Q108	~1	—	1.71	1.57
S316	213	—	2.07	1.95
S542	398	—	2.33	2.20
S633	505	—	2.52	2.42
S712	757	—	2.86	2.73
S936	827	—	2.94	2.84
L210	—	200	1.93	1.8
M213	—	490	2.09	1.97
H218	—	610	2.35	2.22

The concentration of C centres in the nitrogen gettered diamond was estimated from the strength of absorption of a band peaking at 270 nm and the relationship obtained in the work of Davies (1976). It was found to be about 1 ppm. For simplicity, the Q108 sample is referred to in this article as nitrogen free. In annealed diamonds nitrogen was found exclusively in the form of the A centres (nitrogen pairs).

2.2. Raman experiment

Raman spectra of diamonds were studied in the right-angle light scattering experiment using an argon ion laser operating at 514.5 nm with a power of about 150 mW. The experiments were carried out at room temperature. Some samples had significant green light absorption. This is why we used reflecting geometry as shown in figure 1, where the 'I' label corresponds to the incident laser beam focusing in the sample (S) and 'F' denotes the lens collecting the scattered light. A double monochromator DFS-24 was used for the analysis of the scattering light spectrum. The input and output slits were chosen to be 20 μm that corresponds to a theoretical value of 0.35 cm^{-1} for spectral slits. In order to obtain a real experimental resolution of the experimental set-up including the effects of possible aberrations and distortion by the optical system of the double monochromator, finite laser line width etc, we measured the contour from an elastic scatter (a piece of white paper). This contour is shown in figure 2 by the dotted line. The experimentally defined full width at half maximum (FWHM) of the instrumental profile was about 0.6 cm^{-1} . We found that the instrumental profile can be well described by a Gaussian with the corresponding width of 0.53 cm^{-1} . The Raman spectrum from 1320 to 1350 cm^{-1} was measured a few times for every diamond sample from our set. Note that every spectrum was treated independently in order to avoid a broadening due to some 'backlash' for the absolute frequency at reverse motion of the monochromator position (typical possible backlash was about 0.2 cm^{-1}). The cycle of the Raman scattering experiment over the whole set of diamond samples was repeated four times in order to check the reproducibility of experimental results.

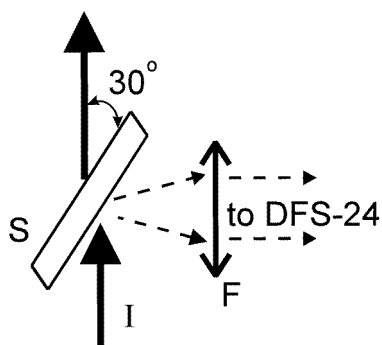


Figure 1. Optical scheme of light scattering experiment.

3. Results

The Raman line in diamonds is centred at 1332.5 cm^{-1} . Figure 2 presents the spectrum for a nitrogen-free sample (symbols) and its description by a Lorentzian contour with FWHM $\gamma_L = 1.65\text{ cm}^{-1}$ (solid line). The magnitude of the FWHM is the same as that typically reported for experiments in pure diamonds with a similar magnitude of the spectral slit

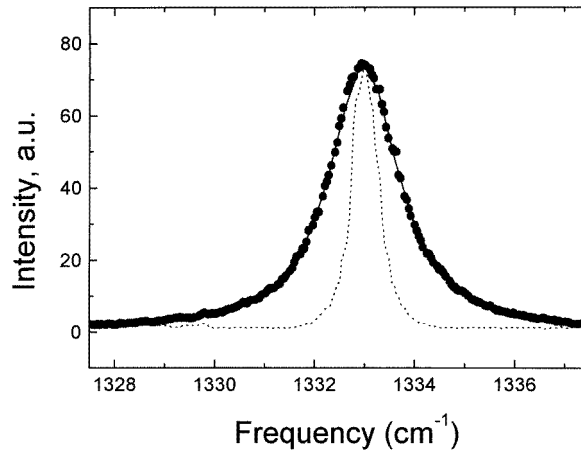


Figure 2. Raman spectrum of a nitrogen-free sample (symbols) and its description by a Lorentzian (solid line) with $\gamma_L = 1.65 \text{ cm}^{-1}$. The dotted line is an experimentally measured instrumental profile of the spectrometer with the used slits.

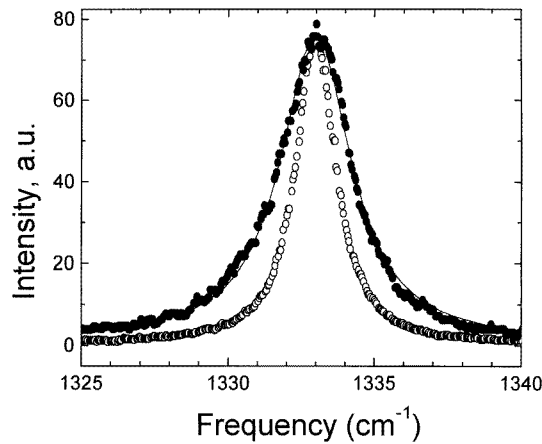


Figure 3. Raman spectra of the sample with high nitrogen concentration 'S936', (solid circles) and its description by the Voigt contour with $\gamma_G = 0.53 \text{ cm}^{-1}$ (instrumental profile) and $\gamma = 1.85 \text{ cm}^{-1}$ (true Raman line width). The open circles correspond to the nitrogen-free sample.

(see e.g. Anastassakis and Burstein 1970, Solin and Ramdas 1970, Washington and Cummins 1977). A representative Raman spectrum of a diamond with high nitrogen concentration is shown in figure 3 by the solid circles. The spectrum of a nitrogen-free sample is shown in this figure by open circles for comparison. It is clearly seen from figure 3 that the Raman line of the nitrogen-containing sample is significantly broader.

From figure 2 it is seen that the instrumental profile is not negligible in comparison with the narrowest experimental spectrum. Thus, for a correct quantitative evaluation, one should take into account the influence of the actual width of the instrumental profile. It is expected theoretically and was demonstrated by measurements with high spectral resolution (e.g., Kirilov and Reynolds 1994) that the true Raman line of an optical phonon is a Lorentzian. Therefore, one should expect a Voigt contour for the experimentally recorded spectrum.

In order to extract the Raman line width, γ , that corresponds to zero slits of the monochromator, we fitted the experimental spectra by the Voigt contour using a standard procedure in the program 'Microcal Origin 4'. Every spectrum was fitted independently using the fixed parameter of the Gaussian contour corresponding to the instrumental profile and being equal to 0.53 cm^{-1} . An example of the fit is shown by the solid line in figure 3 for the sample with high nitrogen concentration. The magnitude of γ extracted from the treatment for any sample in different Raman measurements was the same with a precision of about 0.1 cm^{-1} . Table 1 presents the averages of γ from the results of fitting by the Voigt function for the studied diamonds. For comparison, results for the description of experimental spectra by the Lorentzian contour are also presented in table 1.

The Raman line position can be also extracted from the fits. We observed a rather systematic change of the peak position with the nitrogen concentration in diamonds up to about $0.5\text{--}0.7 \text{ cm}^{-1}$ for the our extremes of the impurity content. However, a systematic study of this effect was complicated by the frequency 'backlash' of the spectrometer. Another problem, which should be taken into account in an analysis of the change of the peak position, is elastic strains, which induce by themselves a Raman line shift. These strains can be an internal feature of the samples as well as being laser induced (see, for example, Lipp *et al* 1997). Thus, the question of the peak position shift with the impurity content for such a small effect (about 0.5 cm^{-1}) is complicated and, since a small shift of the peak has no influence on the results and conclusions of the present study, will not be discussed in the present paper.

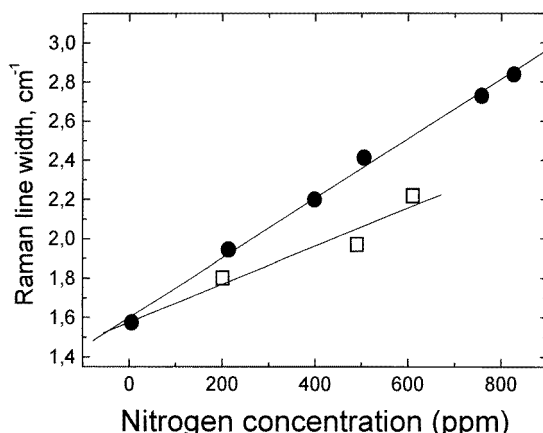


Figure 4. Correlation between the FWHM of the Raman line and the nitrogen concentration. The solid circles correspond to diamonds with C defects; the open squares to crystals with A defects. The solid lines are linear fits corresponding to equations (1) and (2).

A correlation between the experimentally found FWHM of the Raman line and the nitrogen concentration is shown in figure 4. The solid circles in the figure present samples with C defects. The open squares correspond to samples with A defects. From figure 4 it is seen that there is a linear relation between the nitrogen concentration and the Raman line width. In the case of the C centres the linear fit for this correlation, shown in figure 4 by the solid line, is

$$1.60 + 1.52 \times 10^{-3} N \text{ cm}^{-1}. \quad (1)$$

In the case of the A centres, the linear fit is

$$1.57 + 0.97 \times 10^{-3} N \text{ cm}^{-1} \quad (2)$$

where N is the nitrogen concentration in ppm.

These linear fits give a very good description of the experimental data, especially for the set of diamonds with the C form of nitrogen. In the case of the samples with nitrogen pairs the fit in figure 4 is also good, but the scatter of experimental points is greater, probably due to the worse homogeneity of these samples. Note that the constant in the linear relations corresponding to the nitrogen-free samples is the same as can be estimated from previous experiments with nominally pure diamonds, taking into account the actual spectral slits used. The Voigt contour description leads to typical values in the range from 1.5 to 1.6 cm^{-1} for the data from Anastasskis and Burstein (1970), Solin and Ramdas (1970), Washington and Cummins (1977).

4. Discussion

A broadening of the Raman line means a shortening of the phonon lifetime or the phonon mean free path. In other words, the probability of a phonon scattering or relaxing increases. The nitrogen impurity forms centres that disturb the diamond lattice. Therefore, the mean free path of phonons becomes shorter as they undergo additional scattering on these defects. In the case of low impurity concentration, the probability of a phonon scattering on these centres is proportional to their concentration (Gurevich 1980). Hence, the additional broadening of the Raman line is expected to be proportional to the nitrogen concentration. Indeed, from the results of experiment (figure 4), we can see a linear relation between the nitrogen content and the linewidth of the optical phonon spectrum. The linear relation is found for both A and C defects.

It is observed (figure 4) that the Raman line width increases faster as the nitrogen concentration increases in the case of diamonds with C defects. When comparing the strength of interaction between a nitrogen centre and an optical phonon, one should take into account that the A centre consists of two adjacent nitrogen atoms, whereas the C centre is one nitrogen atom inserted into the diamond lattice. Thus, the concentration of the A defects is half the nitrogen concentration. So, from equation (2) the linear fit for the Raman line width has the slope of 1.94 cm^{-1} ppm as a function of the content of A defects—1.28 times higher than for the C defects. Therefore, we can conclude that nitrogen pairs scatter optical phonons slightly more strongly, by about 1.3 times, than single nitrogen atoms.

Let us compare our results with the structural study of diamonds. It is known that the diamond lattice parameter a_0 depends on concentrations and aggregation states of nitrogen impurity. For a relatively low nitrogen content the dependence can be also described by a linear fit, with a slope which is different for diamonds with the A and C forms of nitrogen (Lang 1994). Taking into account the most recently determined relationships between the nitrogen concentration and infrared absorption (Kiflawi *et al* 1994, Boyd *et al* 1994), one obtains from data discussed in the review by Lang (1994) that $\Delta a_0/a_0 = 0.12 \times 10^{-6} N_C$ and $\Delta a_0/a_0 = 0.09 \times 10^{-6} N_A$ for the C and A forms of nitrogen, respectively. Since the A defect consists of two nitrogen atoms, the relative change of the lattice constant becomes $\Delta a_0/a_0 = 0.18 \times 10^{-6} n_A$, where n_A is the concentration of the A defects. A comparison of the results for the two types of defect reveals that the macroscopic dilatation of the whole crystal per defect is 1.5 times higher for the A defect than for the C defect. Qualitatively, this result is similar to our conclusion that the impurity-induced broadening of the Raman line is 1.3 times stronger for the A defect in comparison with the C one.

To our knowledge, there are no theoretical predictions on the interrelation between the Raman line width and the impurity-induced dilatation of the diamond lattice. However, the obtained correlation between the effects of nitrogen centres on the lattice parameter and on the Raman line width is well accepted intuitively, as can be demonstrated by the following

simple speculation. Nitrogen defects distort the crystalline host. The macroscopic dilatation of the lattice, ΔV , is proportional to the concentration of defects, N , and to the distorted volume around a nitrogen centre, V_{dis} . Hence, for the change of the lattice parameter the estimation is $\Delta a_0/a_0 = \Delta V/3V \propto NV_{dis}$. Thus, if we consider the ratio between the slopes of Δa_0 versus N , corresponding to the A and C defects, α_{lat} , we obtain $\alpha_{lat} \propto V_{dis,A}/V_{dis,C}$, where $V_{dis,A}$ and $V_{dis,C}$ are V_{dis} for the A and C centres, respectively. On the other hand, the cross-section of phonon scattering is proportional to the surface of plane projection from a distorted volume around a point defect (Gurevich 1980). In this case, the nitrogen-induced broadening of the Raman line, $\Delta\gamma$, is obtained to be proportional to the number of defects and $V_{dis}^{2/3}$. Hence, the slope of the linear dependence of $\Delta\gamma$ versus the defect concentration is determined by $V_{dis}^{2/3}$ of a centre. If we consider the ratio between the slopes of the A and C defects, α_{Ram} , we obtain $\alpha_{Ram} \propto V_{dis,A}^{2/3}/V_{dis,C}^{2/3} \propto \alpha_{lat}^{2/3}$. Taking the experimental value $\alpha_{lat} = 1.5$, the present consideration predicts $\alpha_{Ram} \approx 1.3$, which coincides with that obtained in our experiment.

In spite of the remarkable coincidence between the estimation and the experimental result, the above speculation uses an oversimplified approach and should be considered rather as qualitative. Nevertheless, the presented consideration has the correct qualitative predictions:

- (i) The linear dependence of the lattice parameter and the broadening of the Raman line on the concentration of defects have very similar slopes for the A and C forms of nitrogen impurity. These slopes for the A defects is slightly higher than for the C defects.
- (ii) The parameter α (the ratio between the slopes of linear relations taken for different kinds of nitrogen defect) for the Raman line broadening is slightly lower than that for the lattice parameter.

5. Conclusion

In the present work the dependence of the Raman spectrum of diamonds on the nitrogen defect concentration was measured in a broad range of the impurity content. Crystals with two types of nitrogen defect, A and C, were used in the light scattering experiment. A linear relation was found between the impurity concentration and the Raman line width. It was established that the slope of the linear fit depends on the type of nitrogen defect. A comparison of these slopes leads to a conclusion that the A centres interact about 1.3 times more strongly with optical phonons than the C centres. A correlation between the dependence of the lattice parameter on the type and concentration of nitrogen impurity and the Raman line broadening is revealed. A possible qualitative explanation of this observation has been proposed.

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