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Chapter 1

Spectral Distribution of SiV centers in Nanodiamonds

In this chapter we report on our results regarding luminescence properties of SiV centers. The samples used in our investigation consists of a large set of CVD nanodiamonds containing *in-situ* SiV centers of a size in the range of 70 nm to 100 nm. Throughout the chapter we refer to samples using their distinct sample-id as listed in ??.

The obtained fluorescence spectra of SiV centers show that both the center wavelength of the ZPL as well as the linewidth of the zero-phonon-line vary strongly among different samples. Our measurements over a large set of SiV centers indicate a strong correlation between the center wavelength of the zero-phonon-line and the corresponding linewidths, resulting in a previously unreported bimodal distribution. We assert single photon emission from these SiV centers across the whole range of zero-phonon-line positions and linewidths. Furthermore we detect fluorescence intermittency, i.e. blinking. The obtained data for the bright and dark times indicate an exponential decay of the dark state and a log-normal decay of the bright state, the latter of which has to our knowledge not been reported as of yet.

1.1 Photoluminescence spectra

To identify nanodiamonds containing SiV centers, we performed confocal scans of the samples. To reduce bias in the measurements, not only the brightest spots of the confocal scans are investigated, but also those which barely exceed background fluorescence. SiV centers are further investigated by measuring photoluminescence (PL) spectra, single photon statistics and photostability. As discussed in ??, the typical luminescence spectrum of an SiV center is composed of a prominent zero-phonon-line peak and weak sidebands. Investigations of both are reported independently in the following paragraphs.

1.1.1 Zero-phonon-line

The center wavelength and the linewidth of the zero-phonon-line (ZPL) of SiV luminescence spectra for samples insitu50, insitu70, and insitu100 are determined by fitting a Lorentzian

fit to the ZPL. Both spectra from single and multiple SiV centers are taken into account. In Figure 1.1 the linewidth for each measured ZPL is plotted against its center wavelength.

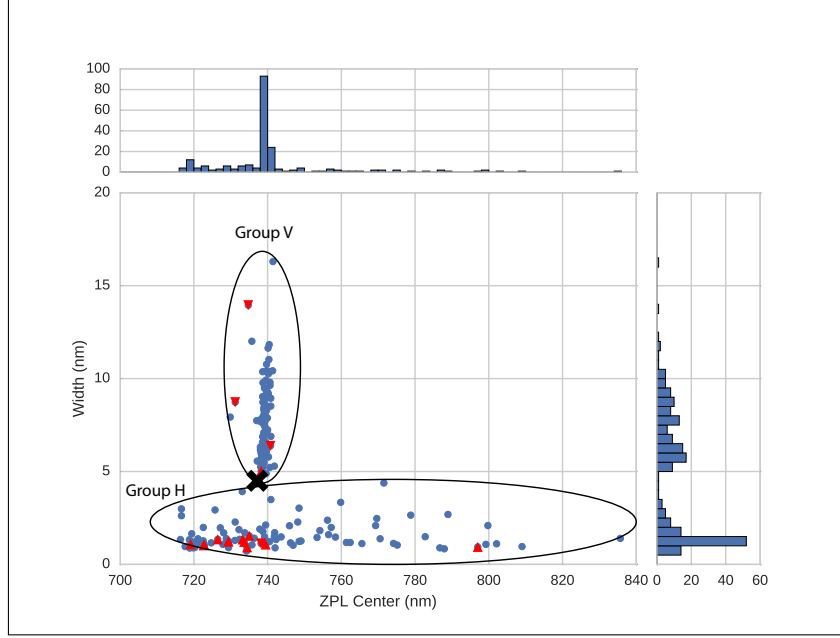


Figure 1.1: Distribution of the ZPL center wavelength versus the linewidth of the ZPL of the investigated SiV centers in milled nanodiamonds containing *in-situ* incorporated SiV centers for samples insitu50, insitu70, insitu100. The data separates into a horizontal (group H) and a vertical (group V) cluster. The bold black cross marks the position of an ideal SiV center in unstrained bulk diamond [?]. The red triangles indicate emitters with an antibunching dip in the $g^{(2)}(0)$ measurement. Upwards pointing triangles represent blinking emitters (fluorescence intermittency), while triangles pointing down represent non-blinking emitters (see ??).

What immediately strikes the eye is a pattern that to our knowledge has not been reported to date: The observed ZPLs partition into two groups, denote a horizontal lobe (group H) and a vertical lobe (group V). The two lobes are separated by a gap, i.e. a region with a pronounced lack of data points. Single emitters are identified both in group H and group V, marked as red triangles in Figure 1.1. Further details on single emitters are given in section ??.

The two groups are defined by their characteristic center wavelengths and linewidths: In group H very prominent ZPL peaks are found showing linewidths in the range of 1 nm to 5 nm and center wavelengths in the range of 715 nm to 835 nm. Figure 1.2a shows a representative spectrum of a single emitter in group H (denoted emitter H1), exhibiting a ZPL line width of 1.4 nm and a center wavelength of 726.5 nm. In contrast, in group V, the spectra exhibit broader ZPL linewidths of approximately 5 nm up to 18 nm. Their ZPL center wavelengths, however, are distributed within the very narrow range of 738 nm to 741 nm. Figure 1.2b shows a spectrum of a single emitter of group V (denoted emitter V1) with a ZPL linewidth of 6.4 nm and a center wavelength of 740.8 nm. For comparison, the room temperature ZPL of SiV centers in unstrained bulk diamond exhibits a linewidth of 4 nm to 5 nm and a center wavelength of 737.2 nm marked with a black cross in Figure 1.1 [?, ?].

To determine how much the ZPLs contribute to the total observed emission of emitter H1 and emitter V1, we determine the Debye-Waller factors for both. The Debye-Waller factor

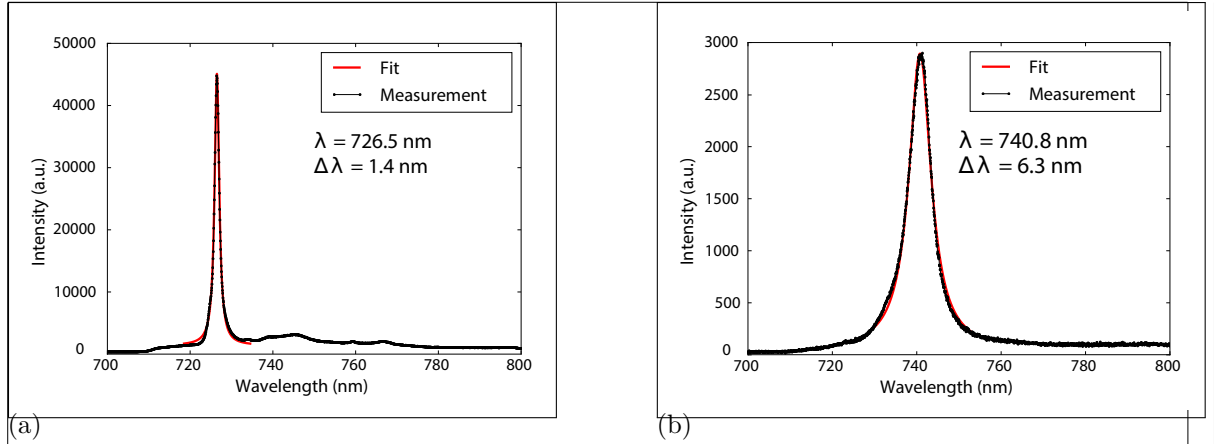


Figure 1.2: Representative photoluminescence spectra of sample insitu100ao measured at room temperature. (a) Spectrum of group H of Figure 1.1, denoted emitter H1. (b) Spectrum of group V of Figure 1.1, denoted emitter V1. The red lines are Lorentzian fits to the peaks.

is defined by $DW = I_{ZPL}/I_{TOT}$ and is therefore suited as a measure for sideband intensity. The Debye-Waller factor for emitter H1 amounts to 0.81 ± 0.01 (given uncertainty due to fit). This Debye-Waller factor corresponds to a Huang-Rhys factor $S = -\ln(DW)$ [?] of 0.21 ± 0.01 , which is in good agreement with the values reported in [?]. The error is mainly due to background corrections. When zooming in onto the spectrum of emitter V1 we do not find distinct sidebands peaks, i.e. almost all emission for this emitter is allotted to the ZPL. Considering resolution limits of the spectrometer, darkcounts and fluorescence background, we evaluate the Debye-Waller factor to be larger than 0.97. It is the largest Debye-Waller factor amongst all our milled SiV centers. The two mentioned Debye-Waller factors should not be interpreted as single representative emitters for the respective groups, they rather serve as an orientation of the spread of the Debye-Waller factors of both groups. It has to be pointed out, that we did not find any systematic difference of the Debye-Waller factor between group H and group V.

To provide context for the novel findings presented in Figure 1.1, we compare our results to various earlier findings. Furthermore, we discuss an additional comparison to an investigated control sample fabricated using silicon implantation. The results are presented in Figure 1.3.

Samples for which previous data has been taken are:

1. nanodiamonds produced by bead-assisted sonic disintegration (BASD) of polycrystalline CVD diamond films (blue rings in Figure 1.3 [?]; data taken from [?])
2. nanodiamonds produced directly via a CVD process with *in-situ* incorporated SiV centers; measured in a spectral filter window of 730 nm to 750 nm (blue squares in Figure 1.3; data reused from [?] with permission)
3. nanodiamonds produced in the same manner as the CVD sample in 2 (blue downwards pointing triangles in Figure 1.3; produced by M. Schreck [?]; spectroscopic measurement performed with setup described in ??)

All previous data from different nanodiamond material fit nicely with the ZPL distribution presented in Figure 1.3, confirming the findings of Figure 1.1.

We verify that the observed luminescent defects are indeed silicon related by performing con-

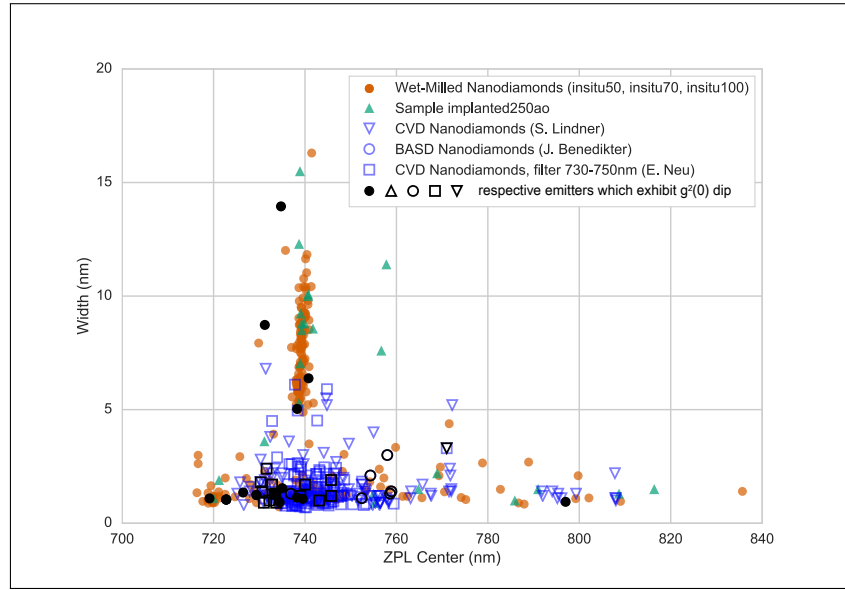


Figure 1.3: Comparison of the distribution of the linewidth vs. the center wavelength of the ZPL of the investigated SiV centers in milled nanodiamonds (samples insitu50, insitu70, insitu100) with data measured on sample implanted250ao (implanted with Silicon); with data measured in our group on CVD nanodiamonds produced by M. Schreck [?]; with data measured on nanodiamonds reported by J. Benedikter in [?]; and with data measured in CVD diamonds by E. Neu in a filter window between 730 nm and 750 nm [?]. Black symbols represent emitters exhibiting a dip in the $g^{(2)}(0)$ function, indicating a single or very few SiV centers

trol experiments with silicon implanted samples (sample implanted250ao). By doing so we rule out the possibility that the two lobes in the distribution are a result of artifacts. Such artifacts include other elements incorporated into the nanodiamonds during the growth process: Residue from previous processes performed in the diamond growth chamber or material from chamber parts may be incorporated during nanodiamond growth. Figure 1.3 shows that the implanted SiV centers cover roughly the same spectral range as the *in-situ* incorporated centers from around 720 nm to 820 nm as the *in-situ* incorporated centers. This correlation provides strong evidence for the silicon related origin of the defects.

To provide a theoretical interpretation, the ZPL center wavelength shift is investigated in further detail and compared to results from density functional calculations. Zooming in to group V (Figure 1.4a) it becomes clear that only six of the measured data points in group V are situated at a shorter center wavelength than the point attributed to an ideal SiV center in unstrained bulk material. The the shortest wavelength shift is at 729.9 nm. At the same time, much more data exhibit a center wavelength bigger than the ideal SiV center. This asymmetry suggests that a red-shift of the ZPL of an SiV center is significantly more likely than a blueshift.

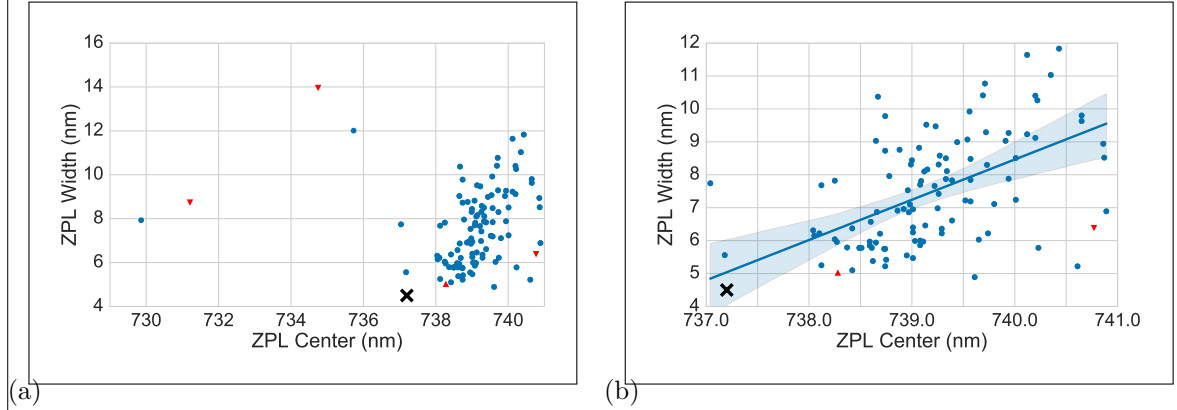


Figure 1.4: (a) A zoom into group V. While many data points exhibit higher center wavelengths (i.e. a redshift) than the ideal SiV center in bulk, only few exhibit shorter center wavelengths (i.e. a blueshift). (b) Zooming further into group V, a clear trend of broader ZPL linewidths for larger ZPL center shifts is visible. The line is a linear regression to all datapoints between 737 nm and 741 nm which exhibit a linewidth bigger than 4 nm.

Several mechanisms contribute to the center wavelength shift, predominantly hydrostatic- and material strain. As explained in ??, we measured the Raman shift of samples insitu70 and implanted250ao. These measurements indicate strain in the diamond lattice in the range of -8.56 GPa to 4.26 GPa. Figure 1.5 shows results from density functional calculations. The shift of the ZPL is modelled in dependence of pressure in the diamond lattice both for hydrostatic stress and for uniaxial stress. Figure 1.5 illustrates that the assumption stated in ??, namely that the strain in the nanodiamonds is due to hydrostatic and uniaxial stress, corresponds well with the measured ZPL shifts in group V.

With higher uniaxial pressure, the ZPL becomes more and more red-shifted. The blueshifted ZPL center wavelengths are explained by hydrostatic stress in the diamond material. The strain calculated from the Raman measurements corresponds well with the results in Figure 1.5 for group V. However, the measured shifts in group H are too broad to be solely explained by strain in the diamond. A potential explanation for the very broad distribution of defect

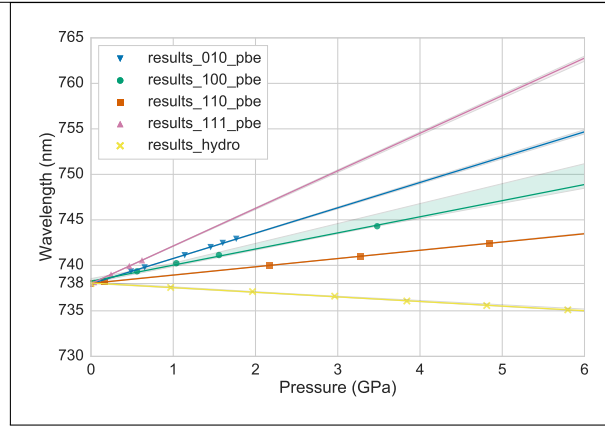


Figure 1.5: Calculations of the wavelength of the SiV center ZPL in dependence of pressure. Markers: calculated pressure with PBE functional; Lines: linear fits to the calculated points, the shaded area around the lines representing the one sigma (68%) confidence interval. Yellow: hydrostatic pressure; other colors: uniaxial pressure, for different orientations. All calculations are performed with a PBE functional. Hydrostatic-type pressure causes a moderate blue shift whereas uniaxial strain causes larger redshift with different magnitudes depending on the direction of the strain

center ZPL center wavelengths could be the association of SiV centers with a further nearby defect, such as a vacancy, or a modified SiV complex such as SiV:H [?].

Zooming in to group V, another effect becomes visible (Figure 1.4b): With increasing ZPL center wavelength, the linewidth becomes broader. As discussed above, a red-shift of the ZPL is linked to increasing uniaxial strain. Thus we conclude that the ZPL linewidth too is affected by strain in the diamond lattice. Here, a modified electron-phonon coupling [?] causes increased uniaxial stress, resulting in larger linewidths. A similar effect has been previously observed for SiV centers at cryogenic temperatures [?].

To conclude, we are able to explain the distribution of ZPL center wavelengths in group V very consistently with theoretical predictions based on perturbative shifts due to strain in the diamond lattice. On the other hand, we have to assume that group H is comprised of modified SiV centers, the structure of which is currently unclear.

1.1.2 Sideband

It is known that the photoluminescence spectra of SiV centers in nanodiamond are dominated by the zero-phonon-line. As a result phonon side band contributions remain small, a fact expressed in large Debye-Waller factors of over 70 % established previously [?, ?]. Our own measurements are consistent with these of emitter H1 and emitter V1 results. We also find distinct sideband peaks in many SiV center photoluminescence emission spectra. The investigated emitters exhibit two different structures of sideband spectra: The spectra in group V exhibit one strong sideband peak, spectra in group H exhibit several weaker sideband peaks. Figure 1.6a and Figure 1.6b illustrate the respective observations.

Most of the spectra in group V exhibit a characteristic shape, composed of the ZPL and one strong sideband peak. 70 % of the photoluminescence spectra with one distinct sideband peak exhibit a shift of the sideband peak from the ZPL between 37 meV to 43 meV. The range of

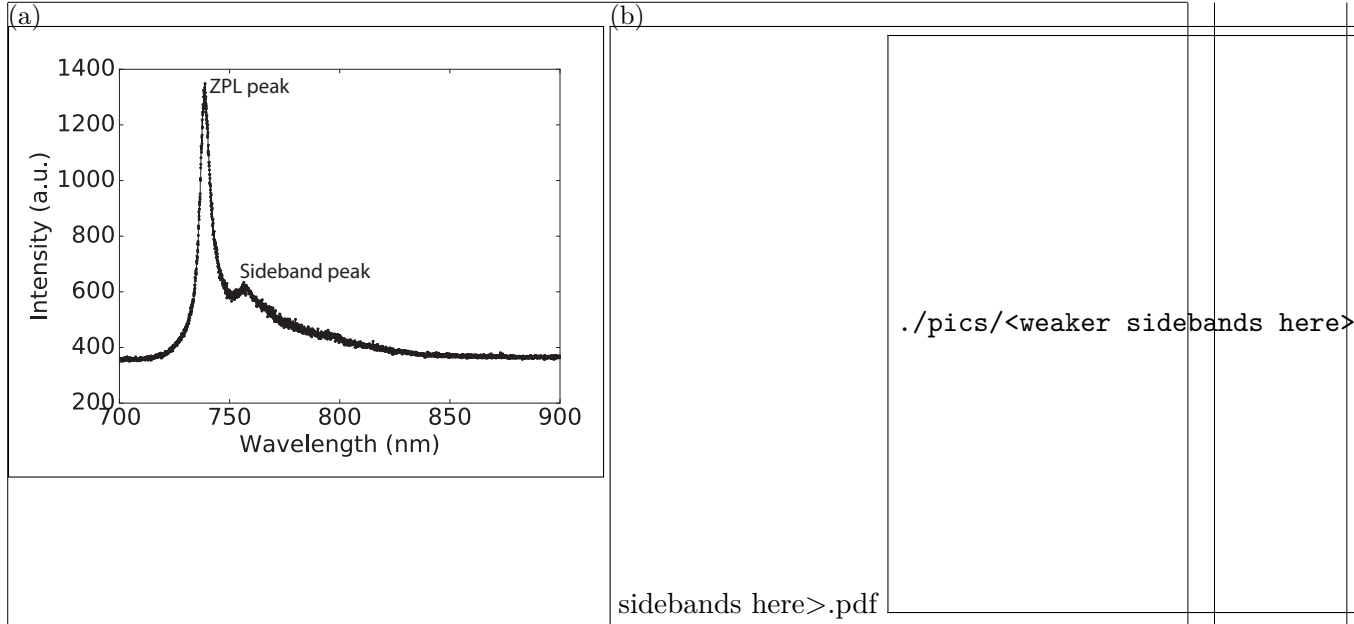


Figure 1.6: Representative spectra of emitters showing single (a) and multiple (b) side band peaks. The former belong to group V, while the latter are members of group H.

line shifts for the prominent sideband peak coincides with a well-known feature at 42 meV, associated with SiV centers [?, ?], but also to a larger number of optically active defects [?]. The occurrence of this 42 meV sideband feature for a large number of defects and the absence of isotopic variations [?], favors an assignment as non-localized lattice vibration. We furthermore observe that the dominant sideband peak shifts towards smaller distance from the ZPL for increasing ZPL center wavelength, i.e. increasing strain. Figure 1.7 presents a linear fit to data for emitters in group V.. The low phonon energy of the sideband feature and its shift with strain might arise from a local “softening” of the crystal lattice in the vicinity of a defect [?].

A recent study [?] suggests that the 42 meV mode, similar to other broad phonon side band features, originates from a resonance attributed to phonons causing the dynamical Jahn-Teller effect with SiV centers [?]. As the Jahn-Teller coupling varies with strain it is also expected that the resonance shifts accordingly.

In the spectra of group V, we do not observe a typical SiV center sideband feature at 64 meV, attributed to a local vibration of the silicon atom, frequently much stronger than the 42 meV sideband peak. A possible explanation is, that the lattice mode at 37 meV to 43 meV is so strong that the local vibrational mode at 64 meV cannot be separated from the tail of the lattice mode.

In group H we observe many spectra which exhibit several peaks within the spectral range of our detection range between 710 nm to 900 nm. The challenge arises to unequivocally distinguish between peaks stemming from a phonon sideband and peaks stemming from shifted, less intense SiV center ZPLs.

Interestingly, we assert a tendency for peaks to accumulate at a shift of around 43 meV, 64 meV, 150 meV and 175 meV. This pattern in the phonon side band of group H is consistent

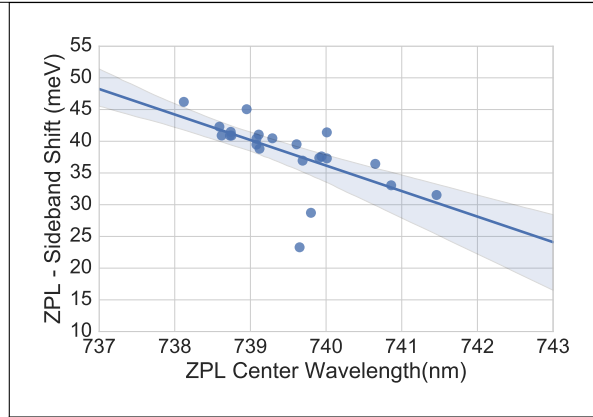


Figure 1.7: Shift of dominant sideband peak from the ZPL in spectra of SiV centers (group V, samples insitu50, insitu70, insitu100) vs. ZPL center wavelength. The linear fit shows that the shift decreases with increasing ZPL center wavelength, i.e. with increasing strain and exhibits a slope of $(-4 \pm 1) \text{ meV nm}^{-1}$. The shaded area is the 95 % confidence region.

with side band shifts reported in [?, ?, ?].

The possibility exists, that some these peaks believed to be phonon side bands are actually shifted ZPLs stemming from other SiV centers. To adress this question, we perform photoluminescence measuerements at cryogenic temperatures.

1.1.3 Cryostatic Measurements

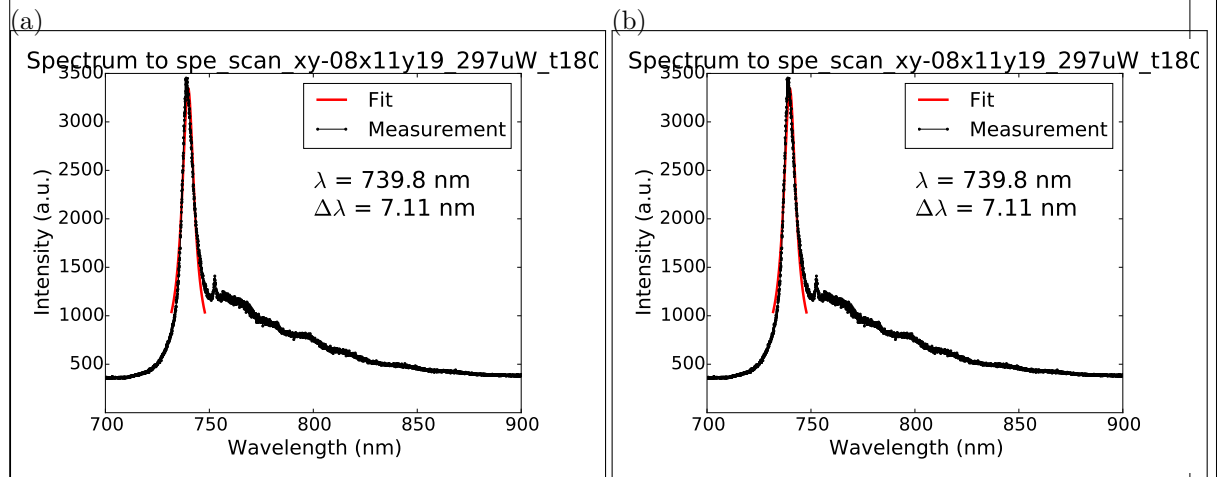


Figure 1.8

Remark:

den teil mit den cryogenic measurments musst du nochmal ordentlich aufschreiben. Hier fehlen noch dinge.

- Wie hast du messungen ueberhaupt machen koennen? Das setup in ?? spricht ja

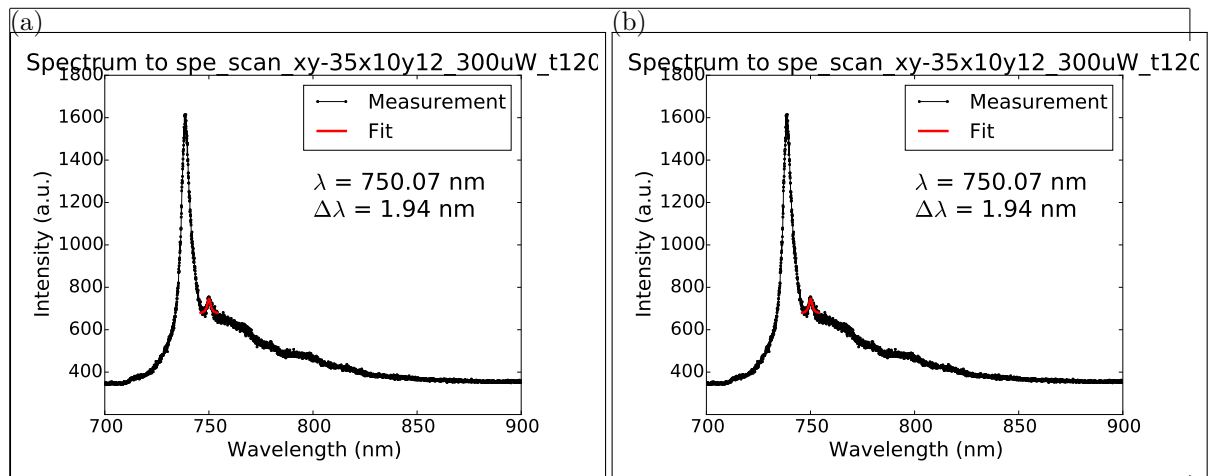


Figure 1.9

nicht von tieftemperaturen. Hast du den aufbau von jemand anderem (janine?) benutzt? Wenn ja dann unbedingt erwahnen. Ansonsten erklaren wie sich der genutzte aufbau vom normalen unterscheidet.

- die bilder die du da bereits eingefuegt hast, die versteh ich nicht. Sind das nur platzhalter und da kommt noch was anderes hin? Ich seh den zusammenhang die geschichte mit der feinstruktur nicht. Das sollte noch geklaert werden.
- wenn man die 4-fach aufspaltung nicht sieht und stattdessen mehrere linien hat, was bedeutet das? Klar ist, man hat kein einzelnens SiV center am start. Abgesehen davon, laesst sich noch was anderes sagen? Wenn man den wood vor lauter lines nicht sieht, dann heisst das auch, dass man nicht sagen kann ob manche der phonon side band peaks von anderen SiV centers kommen oder nicht. Wenn hier keine konklusive aussage moeglich ist, dann sollte das diskutiert werden.
- die sache mit den multiple lines that were strained is mir nicht klar. Soll das heissen die waren verschoben und der grund dafuer war strain? wenn ja, verschoben gegenueber welchem wert, man erwartet ja 4 lininen fuer SiV centers.

We performed some cryostatic measurements to pursue two goals: First, if we see the four-level splitting of the ZPL this is further proof that the dominant peaks of our spectra are indeed all due to SiV centers and do not stem from other impurities. Second, if the sideband peaks vanish at cold temperatures, this is evidence that they are caused by phonons. So we cooled down a sample, but all we saw was a wood of lines. Apparently, there were multiple SiV centers in the nanodiamonds and they were all strained, messing up the four-level line structure.