Chapter 5

SHG and SFG from NiO, a study of charge-transfer excitons

5.1 Introduction

The physical properties of NiO have been studied for more than half a century. Indeed, NiO is an interesting compound: it has a partially filled d-band, and on the basis of the Wilson and Bloch theory of solids [1, 2], metallic behaviour is expected. However, NiO is an insulator, and in 1937 de Boer and Verwey [3] drew attention to this controversial issue. Like Mott and Peierls [4], they argue in their paper, that the repulsive Ni d-d Coulomb interaction could be larger than the kinetic energy gained by delocalization, and, therefore, each Ni ion still has eight 3d electrons and only spin degrees of freedom remain [5]. These are the basic ideas behind the Mott-Hubbard theory [6, 7], according to which an insulating state with a correlation gap is obtained if the d-d Coulomb interaction \( U \) is larger than the d band dispersion width \( W \). So, for some time, NiO was believed to be a prototype of a Mott-Hubbard insulator [8].

However, in 1984 Sawatzky and Allen [9] found from a combined XPS (X-ray Photonemission Spectroscopy) and BIS (Bremsstrahlung Isochromat Spectroscopy) experiment, that NiO has a conductivity gap of 4.3 eV, whereas the Ni d-d Coulomb interaction is approximately 8 eV. They explained the magnitude of the gap by considering NiO to be a so-called charge-transfer insulator. For such materials the energy required to remove a d electron is larger than the energy needed to remove a p electron from an anion, which is then transferred to the cation. The gap edge of NiO is, therefore, due to \( p \rightarrow d \) charge-transfer transitions.

Within the band gap several optically forbidden \( d \rightarrow d \) transitions, in this case Frenkel excitons [11], exist. Due to spin-orbit and phonon effects, they are weakly allowed and can therefore be observed in an optical spectrum. An example of this is the optical spectrum measured by Newman and Chrenko [10] shown in Fig. 5.1.
Keeping in mind the second-harmonic generation (SHG) measurements performed on \( C_{60} \), where an electric-dipole forbidden Frenkel exciton state was probed in a double resonant experiment, NiO appears potentially interesting for a SHG frequency-dependent experiment. We performed such an experiment in the hope to detect the Frenkel-exciton d-d transitions. Moreover, it might be possible to probe it in double resonance with an optically allowed transition above the conductivity gap. These measurements are described in section 5.2. In order to obtain a complete picture, necessary for a proper understanding, we performed also temperature-dependent experiments (section 5.2.2) and sum-frequency generation (SFG) measurements (section 5.2.3). A discussion of the origin of the SHG in NiO is presented in section 5.3.

NiO is a prototype fcc antiferromagnet [12] and has a Néel temperature of 523 K [13]. Recently, Dähm et al. [14] have shown by symmetry arguments, how optical SHG can be used to detect antiferromagnetic spin arrangements at surfaces and in thin films. They discuss in some detail the polarization dependence of SHG arising from the fcc (001) surface of NiO. We followed their suggestions (outlined in

Fig. 5.1. Absorption spectrum of NiO at 300 K and 77 K from Newman and Chrenko [10]. Dashed lines are interpolations.
NiO is also interesting from another point of view. As mentioned above, the conductivity gap is a result of strong electron-electron interactions rather than lattice diffraction effects as in conventional semiconductors like Si. This makes NiO a strongly correlated system of which one of the most salient characteristics is that the electronic structure and properties are extremely dependent on the local electron densities. One might though expect strong nonlinear effects since the system excited by say one photon may have quite a different response to a second photon. In fact there have been predictions of very strong resonance hyperpolarizabilities of Mott-Hubbard like insulators [15]. Although we do not further probe this in detail the background information in SHG discussed here may be of use in future studies of the correlation effects.

Before presenting our contribution to the knowledge of NiO, the excitation spectrum and the magnetic structure of NiO will be reviewed.

### 5.1.1 Excitation spectrum

In the charge-transfer insulator NiO, the eight electrons in the partially filled 3d shell of the Ni$^{2+}$ ion are localized. In contrast to the free ion, the degeneracy of the d levels is partially lifted. The threefold degenerated $t_{2g}$-levels and the double degenerated $e_g$-levels are energetically separated by the cubic crystal-field splitting arising from the six surrounding O$^{2-}$ ions. This is shown in Fig. 5.2 on the left hand side of the excitation spectrum.

The ground state is of $^3A_{2g}$ ($t_{2g}^6e_g^2$) symmetry. The possible on-site (d-d) excitations resulting in both the triplet and singlet excited states, are depicted in Fig. 5.2. The given sequence of states is as calculated by Fujimori and Minami [16], using configuration-interaction method. The same sequence of Frenkel excitons was also found by others, such as Reinen [17]. Fujimori and Minami recalculated the energy states on the basis of the Tanabe-Sugano diagrams [18], derived from crystal-field and ligand-field theory, and obtained comparable results [16]. In the energy level diagram originally proposed by Newman and Chrenko [10] the $^1A_{1g}$ and $^3T_{1g}$ state were interchanged.

In principle transitions between d states are electric dipole forbidden. However, due to vibronic coupling [10, 19], and through hybridization between O 2p- and Ni 3d-orbitals, the dipole selection rules are relaxed and the dipole matrix elements between the d-crystal functions become non-zero [20]. Although the absorption coefficient for d-d transitions is a few orders of magnitude smaller than for the p-d (dipole) allowed transitions at the conductivity gap, they are still observable, as can be seen in the absorption spectrum of Newman and Chrenko in Fig. 5.1.

Another technique, able to probe dipole transitions forbidden in linear optics, is EELS (Electron Energy Loss Spectroscopy) [19]. Since EELS has selection rules
**Fig. 5.2.** Schematic representation of the excitation spectrum of NiO. On the left hand side, the localized picture: the energy level diagram of a Ni$^{2+}$ ion octahedrally surrounded by O$^{2-}$ ions. On the right hand side, the solid-state picture: the charge-transfer interband transitions across the conductivity gap.

Different from those in linear optics, it can provide additional information. Moreover, low energy EELS is surface sensitive, so that surface excitons can be studied, in addition to the bulk ones [21]. Several EELS spectra of the local d-d excitations in NiO have been reported [19, 21, 22, 23]. In particular the work done by Pothuizen exhibits the rich d-d exciton structure within the conductivity gap (Chapter 4 of [21]). Pothuizen also discusses how to enhance features of interest, such as surface phonons and (surface) inner-gap d-d excitons, in an EELS experiment.

On the right hand side of Fig. 5.2, the interband transitions to the electron-hole continuum are indicated. As discussed in the introduction of this chapter, these interband transitions have a charge-transfer character. This means that one electron is transferred from the O$^{2-}$ (2p$^6$) to the Ni$^{2+}$ (3d$^8$) while the electron-hole pair dissociates. The average energy needed for such a process is the so-called charge-transfer energy, $\Delta$, and the conductivity gap is the threshold of such excitations. From combined XPS and BIS measurements the gap is found to be 4.3 eV [9]. Optical absorption measurements, as those done by Powell and Spicer [24], show that the absorption starts at about 3.1 eV and reaches its maximum at 4.3 eV (see also Fig. 5.1). It is generally accepted, that NiO has a conductivity gap of about 4 eV [25], and we adopt this point of view.

The onset of absorption below the conductivity gap (see for instance Fig. 5.1, [24]
Fig. 5.3. A schematic representation of the wave function of the Ni $3d_{x^2-y^2}$-orbital is given in the center of (a) and (b). The O $2\pi_\sigma$-orbitals form in (a) a gerade ligand wave function, giving rise to an optical forbidden transition, whereas in (b) they form an ungerade wave function. For this case the $2p \rightarrow 3d$ transition is optical allowed.

or EELS spectra showing a steep rise in loss intensity above 3 eV [21, 23]) clearly indicates the presence of dipole-allowed transitions at energies smaller than the gap. These transitions can be attributed to charge-transfer exciton. The charge-transfer excitons are bound states formed by the transferred p electron on the Ni$^+$ ion, and the ligand hole on the nearest neighbor O$^-$ ion. Many different charge-transfer excitons are present, since one Ni-ion is surrounded by six O-ions and each O-ion has three degenerate $2p$-orbitals, whereas the Ni-ion has five degenerate $3d$-orbitals. In Fig. 5.3 two examples of the many possible orbital configurations for a charge-transfer exciton are shown schematically. In order to simplify the figure, we consider the two-dimensional case, which can easily be extended to three dimensions. In the center of Fig. 5.3(a) and (b) the $d_{x^2-y^2}$-orbital of the Ni-$3d^8$ ion is depicted. The $p_\sigma$-orbitals of the O-$2p^5$ ions form a ligand wave function of gerade symmetry, when they are oriented as in Fig. 5.3(a). Since the $d_{x^2-y^2}$ wave function has gerade symmetry as well, the O $p_\sigma$-orbitals hybridize with the Ni d-orbital, resulting in a bonding and an anti-bonding state. Due to this hybridization, the gerade charge-transfer exciton state (the anti-bonding state) will be shifted to higher energy (in the conductivity gap). Note that this charge-transfer exciton is due to a $g \rightarrow g$ transition and, therefore, optical forbidden.

On the other hand, the O $p_\sigma$-orbitals shown in Fig. 5.3(b) form an ungerade ligand wave function and hence a transition from the ligand to the $3d_{x^2-y^2}$-orbital is optical allowed. The ungerade ligand wave function does not hybridize with the gerade Ni 3d-orbital, yielding that the charge-transfer exciton in Fig. 5.3(b) is a ”non bonding” state. If the Coulomb attraction between the electron (on the Ni-ion) and the hole (delocalized over the four O-ions) is strong enough, a bound
exciton state can arise below the conductivity gap. De Boer and co-workers [26] calculated that for the case of a bandwidth of 10 eV, a Coulomb attraction of 3 eV is already sufficient to form a bound state below the conductivity gap. For NiO the bandwidth of the $3d^8 \rightarrow 2p^6$ transition is determined by the broad O-bands, and is about 5 eV. Therefore, a Coulomb attraction of approximately 1.5 eV is sufficient to give rise to a bound exciton state below the band. An estimate of the electron-hole Coulomb attraction (or equivalently nearest-neighbour Coulomb repulsion, V) of NiO can be obtained from the data of Tjeng et al. [27]. They found that for Cu$_2$O, V is about 1 eV. NiO, being rather similar in nature, will have a comparable value for V. Therefore, we expect that in NiO there are several optically-allowed, ungerade, charge-transfer exciton states below the conductivity gap. Unfortunately, these charge-transfer exciton states cannot be resolved in a linear optical or an EELS experiment; they are overshadowed by the dipole-allowed transitions at the band edge.

5.1.2 Crystal and magnetic structure

Nickel oxide crystallizes in the rock salt (NaCl) structure. At the Néel temperature ($T_N$) a small rhombohedral distortion from the fcc structure sets in and increases as the temperature is lowered. The distortion consists of a contraction along the [111] direction, and results in a change of the cell angle from being 90° above $T_N$ to 90°4' at 297 K and 90°6' at 78 K [12, 28].

The magnetic structure of NiO is type-II fcc, that is, sheets of ferromagnetically ordered spins within the (111) planes, which are antiferromagnetically stacked along the <111> directions, as shown in Fig. 5.4 [12]. The moments within the (111) planes are oriented in the <112> directions. The contraction occurs in the direction perpendicular to the ferromagnetic layers, indicating that the crystal distortion is directly related to the magnetic structure. An untreated crystal can contain up to 24 distinct kinds of domains. There are four principal, so-called T domains, corresponding to the four body-diagonal <111> directions. For each of these corresponding planes, further three S domains are possible, corresponding to the three possible <112> orientations. From these 12 different spin arrangements another 12 domains can be obtained by time reversal symmetry, which inverts the spin directions [12].

In a thin film the number of domains can be different, since the influence of the surface and the interface with the substrate can provide a direction in which certain domains are more stable than others. For example, in the case of a (100) surface, domains with the long axis perpendicular to the surface are expected to have a different energy than domains with the long axis in-plane. Indeed, using magnetic linear dichroism experiments Alders et al. [29, 30] found that in a NiO film, epitaxially grown on a MgO (100) substrate, a strong preference for domains with a long axis perpendicular to the surface exits. They investigated films with
thicknesses up to 20 monolayers (42 Å), and found only domains with the spins in the eight \([\pm 2, \pm 1, \pm 1]\) directions.

In Chapters 1 and 2 the surface and interface sensitivity of optical SHG for magnetic and non-magnetic systems has been pointed out. Following the approach of Dähm et al., we will treat a special case of the SHG from the surface of the antiferromagnet NiO.

By performing a symmetry analysis of the susceptibility tensor, Dähm et al. show that the SHG signal discriminates antiferromagnetism from ferromagnetism and paramagnetism in a characteristic way [14]. At first sight this is surprising, since both the paramagnetic and the antiferromagnetic states exhibit time reversal symmetry. However, Dähm et al. show that, using different polarizations for the incoming light, the characteristic differences of the susceptibilities in the paramagnetic, ferromagnetic and antiferromagnetic phases can be obtained.

They illustrate this by taking an fcc (001) surface with a spin configuration similar to the one of (001) NiO [14]. Since they do not take the exact spin orientations observed in NiO, their results are not identical to those one would get for the real (001) NiO surface. Due to the inclination of the spin directions (discussed above, see Fig. 5.4), a (001) NiO magnetic surface does not have the 180° rotation along the \(z\)-axis \((2z)\) combined with a translation which was adopted by Dähm et al. for their spin configuration\(^1\). The only non-trivial symmetry element a (001) NiO surface has\(^2\), is \(2x-y = m_{x-y}\), in other words an \((x-y)\) mirror. Since the spins are axial vectors, they will flip under this mirror operation (in the same way as under a time reversal operation). An additional translation is then necessary in order to leave the

\(^1\)In their configuration the spins are oriented parallel to the \(z\)-axis.

\(^2\)This is valid not only for one monolayer, as in the example of Dähm et al. [14], but also if one includes more layers.
system invariant. Thus, $m$ is the point group of the (001) NiO spin configuration.

In this case the non-vanishing tensor elements of $\chi^{(2\omega)}$ are the same as for the ferromagnetic (001) surface configuration $(M|x)^3$. In a SHG experiment in contrast to the claim of Dähm et al., it is not straightforward to separate an antiferromagnetic configuration from a ferromagnetic one even if different polarizations of the fundamental light are used. However, comparing the antiferromagnetic with the paramagnetic configuration, it can be shown that there are some non-vanishing tensor elements in the antiferromagnetic phase, which are not present in the paramagnetic phase. In the NiO case these non-vanishing tensor elements are: $\chi_{yxy}$, $\chi_{yxz}$, and $\chi_{yzz}$. Since the s-polarized SHG signal vanishes for both s- and p-polarized incoming light in the paramagnetic state, any SHG signal measured in the $s_{\text{in}} \rightarrow s_{\text{out}}$ and $p_{\text{in}} \rightarrow s_{\text{out}}$ polarization combinations must be due to the antiferromagnetic or the ferromagnetic phase. Dähm et al., therefore, predict that the characteristic SHG signal of the antiferromagnetic phase will disappear upon crossing the Néel temperature [14].

In order to investigate the role of the antiferromagnetic spin structure of NiO on the SHG, we measured in $s \rightarrow s$ and $p \rightarrow s$ polarization configuration, and we scanned across the Néel temperature. The results will be presented and discussed in section 5.3.1.

5.2 Experimental results

5.2.1 Sample preparation and characterization

The NiO samples were epitaxially grown on MgO (100) single crystal in the Chemical Physics group of Prof. T. Hibma (University of Groningen). For more details see Ref. [30, 32]. After preparation, the samples were removed and transported to the NLO set-up (described in Chapter 3). This can be done in the case of a NiO (100) surface, since this surface is known to be very inert. Indeed, Alders performed angle dependent XAS (X-ray Absorption Spectroscopy) measurements on NiO (100) samples exposed to air and on in-situ grown NiO samples. He found exactly the same results for both cases [29].

Five NiO samples have been studied by SHG and SFG. Afterwards, the linear transmission spectra of these samples have been measured with a Fourier Transform spectrometer (Bomem). From the interference pattern present in the MIR-VIS region (0.5-3 eV) of the transmission spectra, the sample thicknesses have been determined and found to be 50 nm, 290 nm, 325 nm and 380 nm, respectively. The thinnest sample, the 8 nm film, did not exhibit any measurable interference pattern.

3Compare table 2.1 of [31] after a rotation of the $x,y$ axes over 45° with table 1 of [14].

4The NiO samples of Alders were grown in the same laboratory by the same procedure, described in [32], as the NiO samples used in the NLO measurements.
Both NiO and MgO crystallize in the face centered cubic 'rock salt' structure. The lattice constants are 4.176 Å for NiO and 4.212 Å for MgO. This means that there is a lattice mismatch of 0.85% at the interface of the epitaxially grown NiO film and the MgO crystal [29]. In order to get a feeling for the strain at the NiO/MgO interface in our samples, we did X-Ray Diffraction (XRD) 'area scans' of the samples. From these measurements we learned that the 50 nm thick NiO sample is not yet relaxed. That is, over the entire 50 nm, the in-plane lattice constant of the NiO film is identical to the one of MgO. All other (thicker) NiO samples, 290 nm, 325 nm, and 380 nm thick, showed clear evidence of relaxation; i.e., at a given thickness these samples converted from the MgO lattice constant (in the a-b plane) to the NiO lattice constant. In order to allow the transition between a strained and a relaxed structure, there have to be crystal dislocations and misfits in the transition region [33]. The behaviour in the thicker NiO samples was not a surprise, but we were surprised to find out that the 50 nm film was not relaxed. Based on a thermodynamical model of Tsao [33], we calculated a much smaller critical layer thickness (of strained region), namely, 5 nm, assuming the presence of edge dislocations only, or 11.3 nm, admitting both edge and screw dislocations. The relaxation process of epitaxially grown NiO on MgO is still under scrutiny.

5.2.2 SHG

The frequency-, thickness-, polarization-, and temperature-dependent SHG measurements are presented in this section and globally discussed. A more detailed analysis follows in section 5.3.

Film thickness dependence

The frequency-dependent SHG measurements for NiO films of various thicknesses are shown in Fig. 5.5. The first general point to notice is, that at room temperature in the $s \rightarrow p$ polarization geometry, a second-harmonic resonance occurs between 3.7 and 4.0 eV. The second general point is that the second-harmonic intensity of the 50 nm film is much lower than for the other films. This will be discussed in section 5.3.2. The shift of the second-harmonic resonances with respect to the exact second-harmonic resonance frequency is caused by interference effects. We can exclude that the entire second-harmonic peak structure is solely due to interference for the following two reasons.

First, all NiO films, independently of their film thickness, have a similar second-harmonic peak structure around $2\hbar \omega = 3.85$ eV. This is also evident from Fig. 5.6.

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5 The second-harmonic resonance could also be at $\hbar \omega \approx 1.93$ eV. In section 5.2.3 the SFG measurements will be presented, and from these it follows that the second-harmonic resonance is at $2\hbar \omega$. 
where for each film not only the $s \rightarrow p$ SHG data are shown, but also the $p \rightarrow p$ data.

Secondly, in the case that the interference effects are the main contribution, one would expect to observe that a minimum is followed by an increase in second-harmonic intensity. The SHG data of the 290 nm film, which have been taken up to 4.8 eV, do not show this (Fig. 5.5). Thus, the second-harmonic peak structure shown in Fig. 5.5 is indeed a second-harmonic resonance. From the 8 nm and 50 nm data, which are less affected by interference, the resonance energy can be determined to be $\sim 3.85$ eV (in $s \rightarrow p$ geometry).

The second-harmonic resonance energy being below the conductivity gap of 4 eV, and the absence of any second-harmonic intensity at higher energy, are the first indications that this resonance can be assigned to an excitonic state.

**Different polarization geometries**

The second-harmonic frequency-dependent data obtained in $s \rightarrow p$ and $p \rightarrow p$ polarization geometry are shown in Fig. 5.6 for each film. All the data reported in Fig. 5.6 were taken at room temperature except for the data in Fig. 5.6(f) which are taken at 35 K. The data in Fig. 5.6(f) are plotted to demonstrate that the behaviour of the different polarization combinations at low temperature is very similar.
Fig. 5.6. (a)-(e) Frequency-dependent SHG measured in $s \rightarrow p$ and $p \rightarrow p$ polarization combinations for different NiO film thicknesses at room temperature; (f) same for the 50 nm film at 35 K.

A striking point in Fig. 5.6 is that the $p \rightarrow p$ spectra have a peak maximum at a higher energy than the $s \rightarrow p$ spectra. The difference between the resonance peak position of the $p \rightarrow p$ and of the $s \rightarrow p$ spectra is not the same for all NiO films. This is probably due to interference effects, since different polarization geometries exhibit different interference patterns (see Fig. 4.18). On the average, the position of the resonance peak in the $p \rightarrow p$ spectra is about 55 meV higher in energy than the in $s \rightarrow p$ spectra.

A possible explanation for this behaviour could be, that the $s \rightarrow p$ resonance has more surface-like character than the resonance found in $p \rightarrow p$ geometry. Since incoming $s$-polarized light is more surface sensitive than $p$-polarized light, the second-harmonic response in the $s \rightarrow p$ geometry will contain a larger surface contribution, than in the $p \rightarrow p$ geometry. This is evident from Table I in Koopmans et al. [34], where the occurrence of the resolvable tensor components is shown for a thin film measurement in various polarization geometries. Neglecting induced-bulk contributions, i.e., considering only within the electric-dipole approximation, in the $s \rightarrow p$ geometry the surface tensor component $\chi_{s,\perp \parallel \parallel}$ is probed. We use $\perp$ and $\parallel$ to indicate $z$ and $x,y$, respectively. The $p \rightarrow p$ geometry also includes the surface tensor components $\chi_{s,\parallel \parallel \parallel}$, and $\chi_{s,\perp \perp \parallel}$, and therefore has more out-of-plane character. The more pronounced surface sensitivity in the $s \rightarrow p$ geometry is illustrated by observing the SHG data of the 8 nm film in Fig. 5.6(a). The second-harmonic intensity of
This thin film is much higher in the \( s \rightarrow p \) geometry than in the \( p \rightarrow p \) geometry\(^6\). Moreover, among others, Pothenizen et al. \cite{21, 35} found that excitations shift to lower energy when the surrounding of the Ni ion is altered from NiO\(_6\) for the bulk (\( O_h \) symmetry) to NiO\(_5\) (\( C_{4v} \)) at the (100) surface. This is in agreement with our observation that the more surface sensitive \( s \rightarrow p \) second-harmonic resonance is at lower energy.

**Temperature dependence**

The Second-harmonic resonance curve of the 290 nm thick NiO film has been measured at various temperatures. In Fig. 5.7 the SHG data at room temperature and at 35 K are plotted. The temperature-dependent SHG of the 50 nm NiO film is displayed in Fig. 5.8(a), showing, that the SHG from films of another thickness show similar behaviour upon cooling.

Both sets of data show a blue shift and an enhancement of the second-harmonic

\(^6\)Interference effects can modify the proper ratio between the \( s \rightarrow p \) second-harmonic intensity and \( p \rightarrow p \) SH intensity. However, since the film thickness (8 nm) is much smaller than the wavelength used in these experiments (around 600 nm), the 8 nm SHG data are almost unaffected by interference effects.
Fig. 5.8. (a) Temperature-dependent SHG from the 50 nm NiO film measured in s → p polarization combination. The 50 nm film exhibits similar temperature dependence as the 290 nm film (shown in Fig. 5.7) (b) The peak position of the second-harmonic resonance from the 290 nm film plotted as a function of the temperature. The linear fit through the data points has a slope of $-4.6 \times 10^{-4}$ eV/K. (c) The second-harmonic intensity, measured at the resonance maximum of the 290 nm film, versus temperature. The slope of the linear fit is $-1.9 \times 10^{-4}$/K.

Intensity upon cooling. That the blue shift and second-harmonic intensity increase linearly in temperature is visible in Fig. 5.8(b) and (c), in which the resonance peak position and SH-intensity maximum, are plotted as a function of their temperature. The slope of the linear fit through the data is $-4.6 \times 10^{-4}$ eV/K for the peak position and $-1.9 \times 10^{-4}$ 1/K for the second-harmonic intensity.

For comparison, temperature-dependent SHG data obtained from C$_{60}$ are shown in the inset of Fig. 5.7 (see also Fig. 4.8). The origin of the C$_{60}$ second-harmonic resonance is a Frenkel exciton state (the $^1T_{1g}$ state). The similarity in temperature-dependent behaviour of the C$_{60}$ and NiO nonlinear optical response provides an additional suggestion that the NiO second-harmonic resonance might be of excitonic nature.

The SHG data of the 380 nm NiO film presented in Fig. 5.5 and Fig. 5.6 have been measured with the OPO. In Fig. 5.9 the response of the 380 nm film at lower frequencies, as measured with the dye laser, is shown for T at 300 K and 15 K. The SHG data were taken in the energy range covered by the LDS698 dye (675-715 nm; 1.734-1.837 eV)$^7$. The steep slope in the 300 K data is due to the onset of the

$^7$Since the OPO can not be used in this energy range, as discussed in Chapter 3, these mea-
second-harmonic resonance at about $2\hbar\omega \approx 4.0$ eV (see also Fig. 5.5 and Fig. 5.6). As we have already seen in Fig. 5.7 and Fig. 5.8, the second-harmonic resonance shifts to higher energy for decreasing temperature. This time, however, the 15 K SHG data in Fig. 5.9 reveal a small resonance peak, which corresponds to a little shoulder at a slightly lower energy (3.58 eV) in the room temperature spectrum.

The small peak is only present in the $p \rightarrow p$ polarization combination. The $s \rightarrow p$ and $m \rightarrow s$ spectra do not show any peak structure at low temperature nor a corresponding shoulder at room temperature. It is not clear whether this second-harmonic peak structure is resonant at $\hbar\omega$ or at $2\hbar\omega$. Therefore, the data in Fig. 5.9 are plotted as a function of both energy ranges. Further discussion on the possible origin of this resonance follows in section 5.3.

5.2.3 Sum-Frequency Generation

In a SHG experiment the whole cycle of $\omega_{in} \rightarrow \omega_{in} \rightarrow 2\omega_{out}$ is probed. Therefore, a second-harmonic resonance need not necessarily be a resonance at $2\hbar\omega$, but can also be a resonance at $\hbar\omega$. We have seen an example of this latter case in Chapter 4, where a Frenkel exciton ($1^1T_{1g}$ state) at $\hbar\omega \approx 1.81$ eV was probed resonantly on a C$_{60}$ film in a SHG experiment. This process is double resonant with the electric-dipole allowed $2^1T_{1u}$ state at $2\hbar\omega \approx 3.56$ eV, resulting in a strong SHG enhancement.

Fig. 5.9. Room temperature and low temperature SHG from the 380 nm NiO film measured with the dye laser in $p \rightarrow p$ geometry. Apart from the 'big' second-harmonic resonance at about $2\hbar\omega \approx 4.0$ eV, a small resonance at $\hbar\omega = 1.8$ eV or $2\hbar\omega = 3.6$ eV can be seen at 15 K.
5.2. Experimental results

The line shape of the second-harmonic resonance observed in the $C_{\infty}$ experiment is completely dominated by the electric-dipole forbidden transition at $\hbar \omega$.

In Chapter 6 we will see an example of a SHG experiment on CuCl, in which the second-harmonic resonance is a $2\hbar \omega$ resonance. In that case there will be no question about the resonance being at $\hbar \omega$ or $2\hbar \omega$, since CuCl does not have any states below $2\hbar \omega \approx 3.2$ eV.

The situation is more complicated for NiO. As we have seen in the introduction of this Chapter and in Fig. 5.1, NiO has several electric-dipole forbidden d-d transitions within the band gap. In a SHG experiment, where the fundamental light beam has a typical energy of $\hbar \omega \approx 1.5$-2.0 eV, these d-d transitions can appear as $\hbar \omega$ resonances. That they are electric-dipole forbidden need not be a problem, because they are weakly allowed for instance, due to phonon interactions, and can therefore also be observed in linear optics. Furthermore, some of these states are electric-quadrupole or magnetic-dipole allowed, and, as we know from our $C_{\infty}$ study [34, 36], and from other cases [37, 38], electric-quadrupole and magnetic-dipole transitions can be observed in a SHG experiment.

In NiO at an energy of $2\hbar \omega \approx 3.0$-4.0 eV the onset of the conductivity gap is present. In general the precise onset is assumed to be at 4.0 eV. As discussed in section 5.1.1, the conductivity gap is formed by the $O2p \rightarrow Ni3d$ electric-dipole allowed charge-transfer excitation (see Fig. 5.2). At higher energies there are more electric-dipole allowed transitions, which as a whole form a continuum of states (the so-called electron-hole continuum). Above and below the conductivity gap several charge-transfer excitonic states exist. Thus, also at $2\hbar \omega$ there are sufficient states which can give rise to a second-harmonic resonance.

In order to find out whether the second-harmonic resonance observed in the NiO films is at $\hbar \omega$ or at $2\hbar \omega$, we performed SFG experiments. All SFG measurements were done at room temperature on the 325 nm NiO film, and in $p \rightarrow p$ polarization geometry. As two tunable laser sources we used the OPO in the 595-680 nm (1.83-2.08 eV) range, and the dye laser in the LDS698 dye range (675-715 nm; 1.734-1.837 eV). For each measurement we checked carefully that we were detecting the sum-frequency ($\omega_1 + \omega_2$) signal exclusively, ensuring that there was no admixing of the SHG of any of the two laser beams.

Two distinct SFG experiments have been performed. In the first SFG experiment, both laser beams, $\omega_1$ and $\omega_2$, were tuned simultaneously in frequency, so that the sum frequency, $\omega_1 + \omega_2$, remained fixed at 3.826 eV (324.1 nm), the second-harmonic resonance energy for the 325 nm film. This experiment is depicted schematically in Fig. 5.10(b). If the second-harmonic response is resonant at $2\hbar \omega$, then a constant SFG signal is expected, since the sum-frequency energy remains fixed during this experiment. On the other hand, if the second-harmonic response is resonant at $\hbar \omega$ (thus resonant on an intermediate state at 1.913 eV), the SFG data will show a steep increase towards 1.913 eV and lie on top of the second-harmonic
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Fig. 5.10. (a) SFG where two laser beams, $\omega_1$ and $\omega_2$, are tuned simultaneously in frequency, so that their sum-frequency $\hbar(\omega_1 + \omega_2)$ is kept constant at 3.826 eV. The SHG data are plotted at their fundamental frequency ($\hbar \omega = \hbar \omega_1$). If the second-harmonic resonance in resonant at $\hbar \omega$, both data sets should lie on top of each other. (b) Schematic representation of the SFG measurement performed to obtain the SFG data shown in (a).

The result of this SFG experiment is plotted in Fig. 5.10(a). The dashed line marks the second-harmonic intensity at $2\hbar \omega=3.826$ eV. The SFG data, a bit below and above this line, show a fairly constant value as function of the fundamental laser frequencies $\hbar \omega_1$ and $\hbar \omega_2$. The slight increase towards 1.9 eV, can never explain the steep rise in SHG signal. In Fig. 5.10(a), the SHG data are plotted as a function of $\hbar \omega_1$ (=$\hbar \omega_2$ in the case of SHG) in order to compare them with the SFG data. Note, that the second-harmonic intensity increases by more than a factor of 5, while the sum-frequency intensity only increases by about 1.2, i.e., the SFG data do not lie on top of the SHG data. We can compare these results to a case in which the SFG and SHG data are indeed very similar when there are plotted at $\hbar \omega$, namely the case of the 2 eV resonance in C$_{60}$ (see Fig.15 in Chapter 4). From this we conclude that the resonance is at $2\hbar \omega=3.826$ eV, not at $\hbar \omega=1.913$ eV.

In the second type of SFG experiment one checks whether the SFG data and the SHG data plotted as a function of $\hbar (\omega_1 + \omega_2)$ lie on top of each other. Therefore, a SFG spectrum, over a range of sum-frequency energies, $\hbar (\omega_1 + \omega_2)$, has been measured. In Fig. 5.11 the experiment is shown schematically. The frequency of one laser beam, $\omega_1$, is kept fixed (here: 1.91 eV; 648 nm), whereas the second laser beam...
is tuned in frequency ($\omega_2$) from 1.74 eV to 1.83 eV (677-713 nm). The SFG experiment is repeated at three other fixed values for $\omega_1$, 1.96 eV (631 nm), 2.04 eV (608 nm), and 2.08 eV (595 nm), respectively. Finally, combining all four measurements, a SFG spectrum with $\hbar(\omega_1 + \omega_2)$ varying from 3.65 eV to 3.91 eV is obtained. The outcome is plotted in Fig. 5.12(a) together with the SHG data. The SFG data and the SHG data exhibit the same sum-frequency dependence (thus $\hbar(\omega_1 + \omega_2)$ and for SHG $\omega_1 = \omega_2$) confirming our conclusion, that the second-harmonic resonance in NiO is at $2\hbar\omega$.

In Fig. 5.12(b) the same data as in Fig. 5.12(a) are plotted as a function of $\hbar\omega_2$. The various SFG spectra have different slopes indicating that a possible intermediate state does not play a significant role. The slow increase of the SFG data in Fig. 5.10(a) could be due to the higher efficiency of the sum-frequency process when $\omega_1$ and $\omega_2$ are approaching the same value (as the most efficient SFG process is a SHG). This effect is rather small in this frequency range. The same holds for the SFG data in Fig. 5.12(a). The intensity for the SFG process with $\hbar\omega_1 = 1.96$ eV and $\hbar\omega_2 = 1.83$ eV is higher than for $\hbar\omega_1 = 2.04$ eV and $\hbar\omega_2 = 1.74$ eV, although the $\hbar(\omega_1 + \omega_2)$ is identical for both cases. It is possible that the presence of an intermediate state around 1.9 eV causes the sum-frequency intensity to be enhanced. However, such an intermediate state is definitely not resonant. If this were the case, the electric-dipole forbidden character of this state would dominate the line shape of the second-harmonic resonance, in a way similar to the $C_{\infty}$ case.

5.3 Origin of SHG

In this section the origin of the SHG measured in NiO will be discussed. We will first investigate the influence of the antiferromagnetic spin structure on the SHG. Its macroscopic origin (bulk, surface and interface) will be discussed in the view of
Fig. 5.12. (a) SFG where one laser beam, $\omega_1$, is kept fixed at a certain frequency, and the second laser beam, $\omega_2$ is tuned over the range 1.74 - 1.83 eV. By repeating this experiment with a different frequency for $\omega_1$, a SFG spectrum is obtained, which has a $\hbar(\omega_1 + \omega_2)$ dependence. (b) Same data as shown in (a), plotted as a function of $\hbar \omega_2$ (= $\hbar \omega$ for SHG).

the thickness- and polarization-dependent SHG measurements, and by comparing the SHG from epitaxially grown NiO films with the SHG from a (001) NiO single crystal. In section 5.2.2 we concluded, that the second-harmonic peak measured for the NiO film is a second-harmonic resonance. We will, therefore, also discuss the microscopic origin of this resonance, i.e., we want to identify the excitation which is causing this resonance.

5.3.1 Influence of the magnetic structure on SHG

In section 5.1.2 we have discussed the antiferromagnetic structure of a NiO crystal and of an epitaxially grown NiO film. In analogy to Dähm et al. [14] we have established that in the antiferromagnetic phase of NiO the following tensor elements, $\chi_{yy}$, $\chi_{xx}$, and $\chi_{xz}$ are possibly non-zero, while they vanish in the paramagnetic state. These tensor elements can be probed in a SHG experiment using the $s \rightarrow s$ and the $p \rightarrow s$ polarization configuration. In order to get a feeling for the influence of the magnetic structure on the SHG signal obtained from NiO, we have measured the SHG from the 325 nm NiO film in both the $s \rightarrow s$ and the $p \rightarrow s$ polarization geometries.

At room temperature we could not detect any SHG in the $s \rightarrow s$ or in the $p \rightarrow s$ geometry. The results obtained at liquid nitrogen temperature are shown
5.3. Origin of SHG

Fig. 5.13. SHG from the 325 nm NiO film, measured in the \( s \rightarrow s \) and \( p \rightarrow s \) geometry at 77 K, in order to learn about the antiferromagnetic contribution to the SHG signal.

In Fig. 5.13. In the \( s \rightarrow s \) polarization configuration it was still not possible to measure any convincing SHG. However, in the \( p \rightarrow s \) geometry a weak SHG signal was detected at the resonance energy of the 325 nm film (3.87 eV). The reliability of the signal was verified by measuring the SHG off-resonance (3.78 eV): no SHG signal was detected.

We conclude that the antiferromagnetic structure of NiO gives rise to small SHG. Considering the size of the signal, we do not expect any significant contribution due to the magnetic structure of NiO in the SHG measurements presented in the previous sections.

Another measurement was done to obtain additional information on the contribution of the magnetic structure to the SHG. The SHG from the 325 nm film in \( p \rightarrow p \) geometry was measured while scanning across the Néel temperature\(^8\). The result is shown in Fig. 5.14.

In agreement with the temperature-dependent SHG measurements presented in section 5.2.2, the second-harmonic intensity decreases for increasing temperature. The Néel temperature for NiO is 523 K [13]. The temperature given in Fig. 5.14 was measured at the far end of the heating probe, which is not the actual sample temperature. At 500 K this is about 10 to 20 K off. The SHG data measured during heating show a slight change in slope around 550 K. It is possible that at this point the sample reaches the Néel temperature, indicating some antiferromagnetic contribution to the SHG signal. However, there is another explanation for

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\(^8\)Evidently the \( p \rightarrow s \) or \( s \rightarrow s \) geometry would be preferred, since the tensor elements present in these polarization configurations in the antiferromagnetic phase vanish in the paramagnetic phase. However, since we did not detect any SHG in these polarization configurations at room temperature, it made no sense of using them at higher temperatures.
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Fig. 5.14. SHG from the 325 nm NiO film, measured in the $p \rightarrow p$ geometry while scanning across the Néel temperature (523 K). The irreversibility of the SHG upon cooling is indicative of permanent damage to the NiO film due to oxygen depletion from the NiO film for $T>T_N$.

this slight change in slope. In general around the Néel temperature oxygen is depleted from the NiO film [39]. The observation of a distinct pressure increase at the Néel temperature suggest that this occurs also in our case, which will cause an irreversible decrease of the second-harmonic response. Indeed, we measured a reduced second-harmonic intensity during cooling (Fig. 5.14).

Since the second-harmonic intensity does not change noticeable while crossing $T_N$, we conclude that the antiferromagnetic contribution to the SHG in the $p \rightarrow p$ configuration is negligible, confirming our previous ideas. Instead of acquiring information about the antiferromagnetic structure, we noticed the importance of having stoichiometric NiO for the SHG from NiO. This implies that oxygen is playing a significant role in the SHG process, which is reasonable if one assumes, that the observed second-harmonic resonance is due to a charge-transfer exciton.

5.3.2 Macroscopic origin

A NiO crystal has full cubic symmetry. Therefore, to first order, SHG is expected to originate from the surface only, where the inversion symmetry is broken. This is what Dähm et al. [14] and Hübner et al. [40] discuss in their theoretical papers. Since our NiO samples are films grown on MgO substrates, SHG from the interface is also possible.

Going beyond the electric-dipole approximation, higher order effects, such as
induced electric-quadrupole and induced magnetic-dipole contributions, have to be considered as well. Although these higher-order effects are much weaker than the electric-dipole contributions from the surface (or from the interface), they originate from the bulk implying a much larger effective volume. Koopmans et al. estimated that quadrupole bulk contributions can be of the same order of magnitude as the dipole contributions from the interface [41, 42]. Separation of the various contributions is possible but not an easy matter [43]. In the case of C60, Koopmans et al. [34] succeeded to do so by performing thickness-dependent SHG measurements using different polarization geometries.

Since we were unable to grow NiO films in our set-up, we tried to reconstruct a thickness-dependent SHG spectrum by plotting the resonant second-harmonic intensity of the five different NiO films. We took the values obtained from the SHG measurement performed in the $s \rightarrow p$ polarization geometry, rather than the $p \rightarrow p$ geometry, because in the $s \rightarrow p$ configuration fewer SHG tensor components are involved, which reduces the complexity of the interpretation. The data are shown in Fig. 5.15. A thickness-dependent theoretical fit of the second-harmonic intensity in $s \rightarrow p$ geometry has been performed using the expression for $s \rightarrow p$ SH-reflection,
given in the appendix of Ref. [41]. The fitting parameters were the bulk tensor component $\chi_3^{(Q)}$ (see Chapter 2) along with the surface tensor component $\chi_3^{(D)}$, a ratio of $\chi_{3,\perp\perp}$ and $\chi_{3,\perp\parallel}$, and a phase factor. For more details see Ref. [41]. For the theoretical fit shown in Fig. 5.15(a) surface contributions are allowed. In Fig. 5.15(b) the point (0,0), i.e., zero second-harmonic intensity at zero film thickness, is added to the set of SHG data points. By doing this, one forces the theoretical fit of the second-harmonic intensity to decrease at a very small film thickness, i.e., at the surface. In other words, the importance of the surface contribution is forced to be reduced, thereby enhancing the visibility of the importance of the bulk contribution. For the case of Fig 13(b) it was impossible to obtain a decent fit through the data points, in strong contrast to the findings for Fig. 5.15(a). Therefore, one could conclude that surface and interface contributions are dominant in the SHG from NiO. One needs to be aware thought, that there is a considerable uncertainty in the absolute value of the second-harmonic intensity, inhibiting a direct comparison of measurements done at different time periods.

Despite the difficulty mentioned above, it is clear that the second-harmonic intensity from the 50 nm film is much lower than those observed for all other films. This large difference in SHG can be explained by assuming that at 50 nm the surface and interface contribution are canceling each other. Forcing the fit to include the 50 nm point, still produces a reasonable fit in Fig. 5.15(a), while this is impossible in Fig 13(b).

An interesting point supporting this idea is that the SHG from the 50 nm film increased in time (of the order of weeks) contrary to the observations for the other films, where the SHG signal decreased in time.\footnote{Within a measurement, which means during a time of the order of a day, the second-harmonic intensity remained constant. Over a much longer time period a decrease was observed.} If in the course of time the surface contribution to the SHG decreases due to contamination, the (unchanged) interface contribution will eventually start to dominate. The cancellation for the 50 nm film does no longer occur and this causes the second-harmonic intensity to increase.

Another explanation of the SHG data in terms of macroscopic properties is possible, if we consider the influence of the strain, and the corresponding relaxation, in the NiO films. In section 5.2.1 we already mentioned that the 50 nm epitaxially grown NiO film on MgO is the only sample for which strain was measured by X-ray diffraction over the entire film thickness. The 290 nm, 325 nm and 380 nm films all showed clear evidence of relaxation.

A strained (001) NiO film can be visualized as being made up of tetragonal blocks ($x = y \neq z$), instead of cubic units, as it is the case for crystalline NiO. Although tetragonally strained NiO film has a lower symmetry than crystalline NiO, it still has inversion symmetry. This means that within the electric-dipole approximation, no SHG from the bulk is expected, just the surface and the interface will contribute.

On the other hand, in the thicker NiO films there exists an intermediate region
where the structure gradually passes from the strained MgO lattice constant (in the a-b plane) to the crystalline NiO lattice constant. Since the lattice constant of NiO is smaller than the one of MgO, relaxation means that rows of Ni\(^{2+}\) and O\(^{2-}\) ions have to be inserted. The insertion of ions occurs through edge and screw dislocations. As a result this transition region, where the relaxation gave rise to a stress gradient and to structural defects, lacks inversion symmetry and, therefore, SHG from the bulk is allowed within the electric-dipole approximation. This would explain the large difference in the second-harmonic intensity of the thick NiO films compared to the unrelaxed and homogeneous 50 nm film.

Another observation could be seen as support for this picture. We tried to measure the SHG from a (100) NiO single crystal (commercially supplied [44]), but even at liquid helium temperature we could detect no SHG. Similarly a NiO film and the NiO single crystal were measured in a SHG experiment performed in the group of Prof. Th. Rasing at Nijmegen (the Netherlands). Their laser set-up includes a femtosecond Ti:Sapphire laser, which has a much higher peak power than our nanosecond lasers, and is therefore enhancing the sensitivity to SHG. Indeed, at room temperature, off-resonance and in air, they detected SHG from both the film and the crystal. Their measurements confirmed, that the SHG from the crystal is much weaker than from the epitaxial film. Since a NiO single crystal has inversion symmetry, this observation is in agreement with the idea that the relaxed films show stronger SHG because of an intermediate bulk region missing inversion symmetry.

### 5.3.3 Microscopic origin

The SHG spectra for NiO films with varying thickness shown in Fig. 5.5 prove that the second-harmonic peak structure around 3.9 eV is a second-harmonic resonance and not only an interference effect. However, interference effects cause the resonant energy to shift a few tenths of an eV for the different films. In addition, the SFG experiments demonstrated that the second-harmonic resonance is at 2\(\hbar\omega\) and not at \(\hbar\omega\). So, what is the origin of this resonance, what are possible excitations around 3.8-3.9 eV? In section 5.1.1 we have already mentioned that in this energy region there is an electric-dipole allowed O2p \(\rightarrow\) Ni3d transition, which forms the onset of the electron-hole continuum. Within this energy range also the charge-transfer excitons and the electric-dipole forbidden d-d Frenkel excitons are present. In this section we will discuss these possibilities.

The first question is: are we probing an interband transition or an exciton? The second-harmonic resonance is a few tenths of an eV lower than expected for the \(p \rightarrow d\) interband transition, which could be attributed to our samples, which are films instead of single crystals. A more plausible explanation for the shift to lower energy is, however, that the resonance originates from a surface excitation. Pothuizen \textit{et al.} [35] calculated that the charge-transfer gap, \(\Delta\), for the surface is reduced
compared to the bulk value. For a NiO (100) surface, i.e., for the first monolayer of NiO, they found that its conductivity gap was reduced by almost 1 eV compared to the gap in bulk NiO. However, the reduction of $\Delta$ for the second monolayer is already much smaller than 1 eV. Since NiO is an insulator, we will probe more than one monolayer in our SHG experiment\(^\text{10}\). Assuming that we are probing surface SHG, it would still originate from several monolayers, so that $\Delta$ will be reduced compared to its bulk value, but much less than 1 eV. Hence, the second-harmonic resonance could be attributed to a surface $p \rightarrow d$ interband transition. Nevertheless, we will argue that a charge-transfer exciton is a more probable microscopic origin of the second-harmonic resonance.

If the second-harmonic resonance would originate from the $p \rightarrow d$ interband transition, than at higher energies some SHG signal would be expected, due to the entire electron-hole continuum. However, we measure no SHG at higher energies (see Fig. 5.5). Even after correcting the SHG data for the considerable change of $\epsilon_1$ and $\epsilon_2$ in this energy range, i.e., for the linear absorption around the band gap, the second-harmonic resonance remained.

Moreover, as we already mentioned in section 5.2.2, the temperature-dependence of the second-harmonic resonance in NiO closely resembles the temperature-dependent behaviour of the Frenkel exciton in C\(_{60}\) (see Fig. 5.7). For an interband transition no major temperature dependence is expected, in disagreement with our experimental observations. The temperature-dependent SHG measurements are indicative of an exciton resonance.

From the temperature-dependent SHG study on C\(_{60}\), we have learned that it is essential that a system maintains its coherence during the SHG process. Hence, in the last 'step' of a SHG process, the excited state has to decay to the ground state, still having the same phase, i.e., $k$ value, as with the start of the second-harmonic excitation. For an excitation with an excitonic nature, the 'in-phase' recombination of the bound electron-hole pair to the ground state will have a much higher probability than for a free electron and hole. As we have shown in Chapter 2, an exciton has a single $k$ dependence, namely, the $k$ for the combined electron-hole pair. An interband transition has two $k$ dependencies, because the free electron and hole can move independently in the electron-hole continuum. In addition, both particles are charged and therefore more susceptible to scattering and dephasing processes. The probability that the electron and hole recombine still having the same phase is therefore highly unlikely. We feel that, due to the arguments given above, an exciton will exhibit a larger second-harmonic intensity than an interband excitation.

We tried to regenerate the 380 nm NiO film by annealing the film up to 500-600°C in an oxygen atmosphere. XPS measurements, taken of the sample after

\(^{10}\)For a metal, it might be possible to probe only one monolayer in a SHG experiment.
anneal, showed a clean, stoichiometric NiO film. They showed furthermore that Mg substrate ions had diffused through the film to the surface. When we tried to measure the SHG from the ‘recovered’ sample, no signal was detected. It could be that due to the presence of the Mg ions, the charge-transfer band may be broadened into the gap region. As a consequence the exciton state, which originally was lying below the band gap edge, will be situated within the electron-hole continuum. The exciton can just now dephase as easily as an interband excitation, and this leads to a strong decrease of its second-harmonic intensity. However it is difficult to say what the gap region will look like in this case of strong presences of impurities.

All together, we believe these are indications that the second-harmonic resonance measured in NiO is of excitonic origin. In that case, it could be a d-d Frenkel exciton, located on a Ni$^{2+}$ ion, or a charge-transfer exciton, delocalized over a Ni$^{2+}$ and O$^{2-}$ ion. The charge-transfer exciton appears to be more probable, for the following reason.

All d-d Frenkel excitons close to the conductivity gap are of singlet character (see Fig. 5.2), whereas the ground state had triplet character ($^3A_{2g}$). Since we are dealing with optical transitions, an transition with a spin flip is dipole forbidden.

Up to now, we have always considered the second-harmonic resonance as possibly resonant due to a charge-transfer exciton. However in section 5.1.1 we have seen that below the conductivity gap there are several charge-transfer excitons of various symmetry. All these charge-transfer excitons form exciton bands at slightly different energies. As discussed in Chapter 2, we see in optics only excitons at $k=0$, however, for instance impurities and magnons destroy $k$ being a good quantum number. Consequently, transitions with other $k$-vectors are observable as well, resulting in a broadened spectrum which covers the whole exciton band in the limit of large scattering. Several charge-transfer excitons might overlap to form a single broad spectrum. It is therefore possible that the second-harmonic resonance involves several charge-transfer excitons. In the same line of argument the $s \rightarrow p$ second-harmonic resonance may be assigned to charge-transfer excitons, which have a different symmetry than the charge-transfer excitons probed in the $p \rightarrow p$ geometry.

Finally we refer to the SHG measurement where oxygen is depleted from the NiO film around the Néel temperature (see Fig. 5.14). Due to this depletion the second-harmonic intensity dropped irreversibly. If we consider a charge-transfer exciton as the microscopic origin of the SHG signal, then a reduction of oxygen in the NiO film will indeed directly affect the second-harmonic excitation process and hence the second-harmonic intensity.

Having discussed the microscopic origin of the second-harmonic resonance at about 3.9 eV, it would be nice to consider the small resonance found at low temperature on the 380 nm film and shown in Fig. 5.9 as well. It could be a d-d Frenkel exciton (thus at $\hbar \omega$), it could be another charge-transfer exciton, or it could be a
surface excitation. Since too few measurements have been done to draw any definite conclusion, I leave this issue without further discussion. However, I hope to have provoked some curiosity for a nonlinear optical spectroscopic study of NiO.

5.4 Conclusions

We have studied the second-order frequency-dependent nonlinear optical response from epitaxial NiO films grown on MgO substrates. A second-harmonic resonance was found at about 3.9 eV (in $p \to p$ geometry), i.e., 0.1 eV below the conductivity gap. From SFG measurements we established that this second-harmonic resonance was at $2\hbar\omega$ instead of $\hbar\omega$. We also learned from the SFG experiments, that the influence of the electric-dipole forbidden d-d states as intermediate states in the SHG (or SFG) process is not dominant. The SHG from the 50 nm film indicates that there is contribution from the surface and the interface. However, the 290 nm, 325 nm, and 380 nm NiO films can have additional contributions from the bulk, since these films showed evidence for relaxation of the strained layer in the XRD measurements. The influence of the magnetic structure on the SHG appeared to be negligible. The experiment in which we scanned across the Néel temperature showed signs of oxygen depletion from the NiO film. The lower second-harmonic intensity afterwards indicates the importance of having a stoichiometric film.

The above, in conjunction with the observed temperature dependence of the second-harmonic resonance, and the absence of SHG at higher energies, suggest that the most probable explanation for the second-harmonic resonance is the presence of a charge-transfer exciton (or of several charge-transfer excitons) at 3.9 eV. This would mean that, contrary to other techniques such as linear optics and EELS, a SHG experiment can discriminate excitons from interband excitations. Further support for this point of view could be provided by the following experiments.

A first possible "smoking gun" experiment is to see if by changing the number of free carriers in the film, the second-harmonic resonance is also changing. Due to the increased number of free carriers an exciton will be more screened causing the second-harmonic intensity to decrease in the case of an excitonic resonance. On the other hand, if the second-harmonic resonance is due to free carriers, an increase of their density will cause an increase of second-harmonic intensity. A second experiment would be to measure the second-harmonic resonance as a function of an applied magnetic field. An exciton will show a quadratic dependence, whereas free carriers will show a linear dependence. Unfortunately, since the Bohr radius of a charge-transfer exciton in NiO is of the order of 2 Å, huge magnetic fields are needed to observe any dependence.
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