Chapter 6

CuCl, a model system, and a SHG study of Wannier excitons

6.1 Introduction

In Chapter 4 we have probed a Frenkel exciton in a second-harmonic generation (SHG) experiment on $C_60$, and in Chapter 5 we have studied a charge-transfer exciton in NiO. In both cases we found evidence that an exciton (a bound electron-hole pair) exhibits more second-harmonic intensity than an interband transition (free electron-hole pair). To check the generality of this idea we have studied a third kind of excitons, the Wannier excitons, using a second-harmonic frequency-dependent experiment on CuCl. In linear optical experiments two Wannier excitonic transitions have been readily observed just below the conductivity gap [1, 2]. Furthermore, CuCl is quite useful as a model system for our ideas about the enhancement of the oscillator strength of excitonic transitions in SHG experiments with respect to the interband transitions, because of the existing experimental and theoretical knowledge of the exact position of the exciton energies and of the conductivity gap (interband transitions) [1, 2, 3], and the demonstrated SHG from CuCl [4, 5]. Thus, by performing a second-harmonic frequency scan in the energy range where the excitons and conductivity gap are located, namely $2\hbar \omega \approx 3 - 3.5$ eV, we can verify whether there is indeed an enhancement of second-harmonic intensity at the excitonic energies with respect to the interband transition energies.

There are several reasons why CuCl is a rather well studied material. The Cu halides occupy an important position among the binary semiconductors, since they form the end-points of several isoelectronic series. However, it is impossible to derive the basic electronic parameters of CuCl by a simple extrapolation from the isostructural and isoelectronic sequence Ge, GaP, ZnS and CuCl [1]. The reason is that in contrast to Ge, GaP and ZnS, where the valence bands are dominated by $sp^3$-
hybrids, in CuCl the energies of the metal 3d levels are close to the halogen p-levels. Therefore, a strong p-d hybridization occurs, which significantly alters the physical properties [6]. Hence, in the sixties and seventies the optical and electronic properties of the Cu halides were investigated in order to comprehend their valence band properties [1, 2]. A renewed interest in the electronic structure of CuCl arose at the end of the seventies when magnetic-susceptibility and conductivity measurements suggested that CuCl might be a superconductor [7].

In 1988, Hanamura [8] showed theoretically that the nonlinear optical polarizability can be enhanced greatly in semiconductor microcrystallites. This enhancement is caused by the fact that in a microcrystallite, the exciton becomes quantized due to confinement. Furthermore, the excitons in a single microcrystallite should interact strongly enough to cause the excitons to deviate from ideal harmonic oscillators. CuCl is a typical material for exciton confinement [9], since its excitons have a relatively small Bohr radius (∼7 Å), and a large binding energy $E_{\text{exc}}^b$ (∼190 meV). Hanamura [8] calculated that in the case of CuCl microcrystals of a size of about 64 Å and for $k_BT \ll E_{\text{exc}}^b$, an enhancement of the order of $10^4$ for $\chi^{(3)}$ can be expected. This observation is important from an engineering point of view: materials with a large optical nonlinearity are required for optical shutters or optical information processors [10]. As a result, several papers on the (large) optical nonlinearity of CuCl microcrystals were published in the nineties [9, 11, 12].

Very recently, CuCl has regained interest once more, due to the ability of the excitons in CuCl to form biexcitons, which are possible candidates to undergo a Bose-Einstein condensation. Indeed, Mysyrowicz [13] and Hasuo [14] showed evidence that excitonic excitations in semiconductors like CuCl exhibit features expected in a weakly interacting Bose gas.

In the next section an overview will be given of the existing knowledge about the excitation spectrum of CuCl. The results of our SHG measurements on CuCl will be presented and discussed in the last section.

## 6.2 Excitation spectrum

### 6.2.1 Crystal structure and symmetry considerations

The Cu halides are members of the family of semiconductors with four valence electrons per atom. Among these semiconductors are the elemental semiconductors of group IV of the periodic table (diamond, Si, Ge, and gray tin) which are purely covalently bound and crystallize in the diamond structure type (space group $O_h^h$). The other members of this family are the III-V and II-VI semiconductors. Most of these semiconductors crystallize, under ordinary conditions, in the cubic zincblende
structure type \(^1\) \((T_d^3)\) or the hexagonal wurtzite structure type \((C_{6v})\) \(^2\).

The ionicity of the compounds increases with increasing distance within the periodic table. Consequently, the I-VII compounds are found at the strongly ionic end of the series of tetrahedrally coordinated crystals. Most I-VII compounds, therefore, are octahedrally coordinated and adopt a rocksalt arrangement \((O_h^5)\). Nevertheless, CuCl, CuBr, and CuI also form the zincblende or the wurtzite structure type. This shows that the Cu halides are situated in the region between tetrahedral and octahedral coordination, which may lead to a rather complex phase diagram \(^2\). For CuCl the phase diagram, however, is not that complicated: at ambient pressure, there is only one phase transition at 680 K. Below this temperature CuCl has a zincblende structure, and above the transition up to the melting point (695 K) it has a wurtzite structure \([1, 2, 15]\). Since all our experiments were performed below 680 K, we can restrict our considerations to the zincblende case.

The consequences of the increasing ionicity from the IV to the I-VII compounds are also reflected in their excitation spectra. In the elemental semiconductors the valence band arises from the bonding of the \(sp^3\)-hybrid orbitals, and the conduction band arises from the anti-bonding \(sp^3\)-hybrids. On the other hand, in the case of ionic binding, the valence bands arise from the highest occupied atomic \(p\)-levels of the anions with a more-or-less pronounced mixture with \(d\)-levels of the cation (the metal). The conduction band states come from the lowest empty \(s\)-levels of the cations. For CuCl this means that its valence band is formed by a hybridization of the filled \(3s^23p^6\) noble-gas shell of Cl\(^-\) ions and the \(3d^{10}\) shell of Cu\(^+\) ions. The conduction band of CuCl is predominantly formed by Cu \(4s\)-orbitals \(^1\). Due to the hybridization between the halogen \(p\)-orbitals and the Cu \(3d\)-orbitals, the physical properties of these semiconductors are altered with respect to those of the other families. In particular, their first absorption edge occurs at a much lower energy than expected by extrapolating the corresponding edge of the isoelectronic II-VI compounds \(^1\).

The exciton spectrum of the Cu halides can be interpreted along the same lines as the absorption edge of other materials with wurtzite and zincblende structure type. As shown schematically in Fig. 6.1, in the zincblende structure the top of the valence band \((\Gamma_{15}^2)\) is triply degenerate without spin-orbit splitting. The spin-orbit interaction reduces this degeneracy to a twofold \((\Gamma_8)\) and a non-degenerate \((\Gamma_7)\) state. Coupling of the lowest conduction band state \(\Gamma_6\) to both uppermost valence band holes \(\Gamma_7\) and \(\Gamma_8\) gives rise to the edge excitons \(Z_3\) and \(Z_{12}\), respectively (see Fig. 6.1). The double degeneracy of the \(Z_{12}\) exciton is lifted in strained samples \(^1\).

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\(^1\)Occupation of all zincblende atomic positions with the same atoms would lead to the diamond structure.

\(^2\)\(\Gamma_{15}, \Gamma_6, \Gamma_7, \text{and } \Gamma_8\) are irreducible representations of the space group \(T_d^3\) at the \(\Gamma\) point \([17, 18]\).
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Fig. 6.1. Schematic development of valence states due to s, p and d electrons at the Brillouin Zone center Γ in the cubic crystal field of the zincblende structure (not to scale). Energies given are the experimental values obtained for CuCl [1, 19]. The numbers in brackets indicate the degeneracy of the corresponding state.

6.2.2 Review of linear optical experiments

The absorption and reflection spectra of CuCl are dominated by the \( Z_3 \) and \( Z_{1,2} \) exciton peaks, followed by a rather flat absorption up to about 6 eV, as can be seen in Fig. 6.2. Similar spectra are observed for CuBr, CuI, and AgI. All of them, however, show an inverse order of \( Z_3 \) and \( Z_{1,2} \) peaks, as compared to CuCl. The peak position inversion was the first evidence for the strong Γ-point d-admixture at the upper valence band edge, as already discussed above, and pointed out by Cardona in 1963 [1].

Several other people have measured the absorption and reflection spectra of CuCl films and (micro)crystals. For a review of the various measured exciton energies, I refer to Goldmann (1977) [2] and Hönerlage et al. (1985) [21]. The reported energies, at which the \( Z_3 \) and \( Z_{1,2} \) excitons are observed, all have approximately the same values. Taking the average of the numerical values from the six references given by Goldmann [2], one obtains for \( T<10 \) K, the \( Z_3 \) exciton position at 3.203 ± 0.003 eV and the \( Z_{1,2} \) exciton at 3.273 ± 0.005 eV. The splitting between the \( Z_3 \) and \( Z_{1,2} \) exciton is accordingly 70 ± 5 meV.

Kaifu and Komatsu [22] have obtained exciton spectra from transmittance measurements on thin CuCl films, and from a Kramers-Kronig analysis of reflection measurements on single crystals. They measured the temperature dependence, and
reported that the $Z_{1,2}$ exciton is at 3.297 eV and 3.319 eV at 100 K and 200 K, respectively, while the $Z_3$ exciton is at 3.230 eV and 3.248 eV.

The large absorption coefficient (greater than $10^5 \text{cm}^{-1}$, as indicated in Fig. 6.2(a)) implies experimental difficulties. At such high absorption values, measurements require very homogeneous, stress-free films of thickness $\leq 10^3 \text{Å}$ [2]. For high quality samples (thus, very thin films with single crystal domains), and sufficiently energy resolution, one observes an "excitonic fine structure" as shown in Fig. 6.3 [2, 3]. In addition to the lowest energy state ($n=1$) of the $Z_3$ exciton at 3.205 eV, also the corresponding $n=2$ and $n=3$ lines of a hydrogen-like series are excited at 3.366 eV (2s) and at 3.385 eV (3s). From this fine structure Goldmann extracted, with an accuracy of a few meV, values for the binding energy, $E_b=190$ meV, and hence the band gap, $E_g=3.395$ eV. In a similar way, Saito et al. deduced from their linear and nonlinear spectroscopical studies a band gap energy of $3.3990 \pm 0.0005$ eV [23].

So far, we have reported in a bird’s eye view, what can be found in literature on the linear optical data of CuCl around the band edge. Below, we summarize what is known in literature on the nonlinear optics of CuCl, i.e., a short review is given of SHG, four-wave-mixing (FWM), and two-photon-absorption (TPA) measurements on CuCl crystals.
6.2.3 Review of nonlinear optical experiments

Chemla and co-workers [4] were among the first ones to present a study of the nonlinear optical properties of cuprous halides in the near and mid infra-red. They found second-order susceptibilities comparable in magnitude to those of quartz and GaAs. To explain the large nonlinear susceptibilities of the cuprous halides, d-state effects of the noble metal have to be taken into account. This supports Levine’s bond-charge model [24].

Haukeisen and Mahr [5, 25] measured the frequency dependence of the SHG in the region of the first and second 1s-excitons of CuCl. They clearly found two resonances at 20 K, centered on the 1s-exciton resonances, at 3.204 and 3.268 eV, respectively. However, their SHG data stop at 3.34 eV, therefore they did not probe the onset of the conductivity gap, which we need in order to be able to distinguish a SHG signal due to an exciton (bound electron-hole pair) from the one of a free electron-hole pair.

More recently, spectroscopic SHG data on CuCl were obtained by Fröhlich and Pahlke-Lerch [26]. They measured the nonlinear reflection of the second harmonic at oblique incidence in the reststrahl band of the Z\textsubscript{3} exciton of CuCl crystals. They found not only the transverse exciton at 3.202 eV, but also the longitudinal exciton at 3.208 eV. Their second-harmonic frequency scan went up to 3.213 eV, and thus, they did not probe the conductivity gap as well.

In the field of the third-order nonlinear optical spectroscopy work on CuCl has been done by Kramer et al. [28], and Kramer and Bloembergen [29]. They studied the dispersion of $\chi^{(3)}[-(2\omega_1 - \omega_2); \omega_1,\omega_1, -\omega_2]$ in a four-wave-mixing (FWM) experiment. In this case $2\omega_1$ is equal to the frequency of the first longitudinal exciton resonance. An advantage of this technique is that the applied $(\omega_1, \omega_2)$ and the observed frequencies $(\omega_3 = 2\omega_1 - \omega_2)$ all lie in the transparent region of the material.
investigated. In principle, both the transverse and the longitudinal excitons should be observed in this mixing, but Kramer and Bloembergen [29] found that for the transverse exciton no resonance could be observed, due to an accidental destructive interference. They observed, however, the longitudinal $Z_3$ exciton resonant at 3.208 eV ($T<10$ K). In addition they measured its temperature dependence. For $T>30$ K, they found that the longitudinal exciton energy is linearly dependent on temperature with a slope of $2.9 \cdot 10^{-4}$ eV/K. Referring to Cardona [1], they point out that the sign and magnitude of the slope is determined by a competition between the electron-phonon interaction (explicit temperature effect) and the temperature dependence of the lattice constant (volume effect).

Cardona, suggested that the positive volume effect could be due to a decreased contribution of the metal wave function to the valence band wave function as the lattice constant is increased, which would produce an increase in the energy gap [1]. However, later work shows that the thermal expansion effect is negligible in CuCl, because of the extremely small dependence of the band gap on volume [30]. Garro et al. gave another explanation for the increase of the direct gap of CuCl with increasing temperature, based on the electron-phonon interaction. They suggest that the vibration of the Cu ions leads to an increase in the gap while the opposite is true for the chlorine ions (the latter corresponds to the usual behavior) [31].

Another third-order nonlinear optical experiment is two-photon absorption (TPA). Fröhlich and co-workers [27] were the first to perform two-photon absorption experiments on single crystals of CuCl at 20 K. In Fig. 6.4 their TPA spectrum is shown. In this case the energy range (from 3.2 to 4.3 eV) also includes the conductivity gap. The spectrum reveals the typical behaviour one finds near the gap, which commences at about 3.4 eV. Below the gap edge two sharp exciton lines can be seen. The energies of these lines are at 3.210 eV and 3.292 eV, which agrees quite well
with the exciton lines observed in the single-photon spectrum.

Usually, in systems with inversion symmetry, one- and two-photon transitions are mutually exclusive; single-photon transitions are allowed between states with different parity while two-photon transitions are allowed between states with the same parity. In systems without inversion symmetry, sometimes transitions exist which are both one- and two-photon allowed. For CuCl, all one-photon transitions are also two-photon allowed, but there exist additional two-photon transitions which are forbidden in the single-photon absorption. Longitudinal excitons, for instance, are only accessible by two-photon transitions [30].

Indeed, Fröhlich and co-workers [32] pointed out in later work, that the first two lines observed in the TPA spectrum, which correspond to 1s-exciton states, are longitudinal excitons\(^3\) and that only these states are observable in TPA experiments. This explains the energy differences between the 1s-absorption lines in TPA and SPA (single-photon absorption) clearly observable in the spectrum of Reinmann and Rübenacke, which shows both, SPA and TPA data [30]. Note that this difference between the transverse and longitudinal excitons (5.1 and 174 meV for the Z\(_3\) and Z\(_{1,2}\) excitons, respectively) is actually measured in the SHG experiment of Fröhlich and Pahlke-Lerch [26], already discussed above.

An overview of the energies of the transverse \(Z_3\) and \(Z_{1,2}\) excitons \((Z_{3T}^T, Z_{1,2}^T)\), the longitudinal \(Z_3\) and \(Z_{1,2}\) excitons \((Z_{3L}^L, Z_{1,2}^L)\), and the conductivity gap determined using the various optical techniques is presented in Table 6.1.

Summarizing: based on the data of CuCl already known from literature, we determine that in CuCl the \(Z_{3T}^T\) and \(Z_{1,2}^T\) exciton energies are at about 3.203 eV, and 3.271 eV, respectively, and that the onset of the conductivity gap is at about 3.40 - 3.45 eV. In linear-optical spectra and in two-photon absorption spectra, both the excitons and the band gap are clearly observable. However, these techniques probe incoherent processes, whereas SHG probes coherent processes. This is an important and fundamental difference. We did not find a SHG measurement in the literature, in which not only the excitons, but also the band gap was probed. Therefore, we did this measurement ourself, and the results are presented in the next section.

### 6.3 Measurements on a CuCl film

#### 6.3.1 Sample preparation and characterization

CuCl powder with a purity of 99.995 % (Aldrich) was evaporated at 763 K on a MgO substrate. Since, CuCl is rather reactive and difficult to remove, we decided

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\(^3\)More precisely: longitudinal excitons and transverse polaritons, but such details go beyond the scope of this section. For a review of the exact dispersion of excitons, polaritons and biexcitons in direct-gap semiconductors, including CuCl, please refer to the paper by Hönerlage \textit{et al.} [21].
not to contaminate our entire preparation chamber. The film growth, therefore, took place in a small separate UHV chamber at a pressure of about 1.10^{-6} mbar. Because of the hygroscopic nature of CuCl, the transport of the CuCl film from one UHV system to the other was done under a protective inert gas.

On the same sample, afterwards, also linear-optical measurements with a Fourier Transform spectrometer (Bomem) were performed. From the interference pattern obtained in the MIR-NIR region, the film thickness could be determined: we found that the film was 2.3 \mu m thick. The absorption spectrum also clearly showed the onset of the first exciton at 3.25 eV (at room temperature). However, the unsuitability of the Bomem to measure in UV inhibits the extraction of more reliable information from the linear-optical measurement. Therefore, we used the values for the exciton and band-gap energies found in the literature.

### 6.3.2 SHG measurements

The SHG measurements on the CuCl film have been performed using the dye laser. The following dyes were used: Pyr2 in the range 1.660 - 1.744 eV (711 - 747 nm), LSD759 for 1.627 - 1.676 eV (740 - 762 nm) and LDS765 for 1.590 - 1.653 eV (750 - 780 nm). For all measurements the fundamental ingoing beam was s-polarized, and the second-harmonic reflected beam p-polarized (s_{in} \rightarrow p_{out}).

The result of the SHG measurement taken at 5 K \(^4\) is shown in Fig. 6.5. We

\(^4\)The cryostat temperature is 5 K. From the calibrations already earlier executed for the C\(_{60}\)

<table>
<thead>
<tr>
<th>Technique</th>
<th>T (K)</th>
<th>(Z_3^T) (eV)</th>
<th>(Z_3^L) (eV)</th>
<th>(Z_{12}^T) (eV)</th>
<th>(Z_{12}^L) (eV)</th>
<th>Band gap (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHG oblique refl.</td>
<td>1.5</td>
<td>3.202</td>
<td>3.208</td>
<td></td>
<td></td>
<td></td>
<td>[26]</td>
</tr>
<tr>
<td>SHG transm.</td>
<td>20</td>
<td>3.204</td>
<td>3.268</td>
<td></td>
<td></td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>FWM</td>
<td>15</td>
<td>3.2077</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[28]</td>
</tr>
<tr>
<td>TPA</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>3.203</td>
<td>3.2082</td>
<td></td>
<td></td>
<td></td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>3.2103</td>
<td>3.2928</td>
<td></td>
<td></td>
<td></td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3.210</td>
<td>3.292</td>
<td>(\sim 3.4)</td>
<td></td>
<td></td>
<td>[27]</td>
</tr>
<tr>
<td>Expectation</td>
<td></td>
<td>3.203 (3.208)</td>
<td>3.271 (3.29)</td>
<td>(\sim 3.40-3.45)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHG in refl.</td>
<td>&lt;20</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
clearly see a second-harmonic resonance at 3.287 eV, a sharp peak at 3.21 eV and the start of another second-harmonic resonance situated at about 3.18 eV. No enhancement of SHG was detected around the band gap at 3.4 eV. In the inset the 100 K data are shown, confirming that the steep slope around 3.2 eV at 5 K is indeed due to a second-harmonic resonance.

On the other hand, the very sharp peak at 3.21 eV is no second-harmonic resonance. Haueisen and Mahr [5] observed in their SHG measurements a similar sharp peak between the two exciton lines. They attributed this spike to an accidental single point of near phase matching ($\Delta k = 0$) due to the crossing of the second-harmonic and the fundamental refractive index value, when the second-harmonic photon energy lies between that of the two excitons. Staude [34] calculated the optical constants by a Kramers-Kronig analysis of reflectivity, and he found that at about 3.217 eV (the energy where Haueisen and Mahr observed their sharp peak) the index of refraction has a value of 1.95. This equals to the value of the index of refraction at the fundamental frequency [35].

That our spike is observed at a slightly lower energy than Haueisen and Mahr measurements, we deduce that the corresponding sample temperature is about 25 K.
Fig. 6.6. (a) Temperature-dependent SHG from the CuCl film. In this case the spike, due to single point phase matching present in Fig. 6.5, has been removed from the 5 K and 100 K spectrum. (b) Central resonance energy and (c) second-harmonic intensity (peak maximum) of the $Z_{3}^{T}$ exciton plotted as a function of temperature. The straight lines are linear fits through the data points.

(3.21 eV versus 3.217 eV), can be easily explained. Our lowest second-harmonic resonance is found at a somewhat lower energy as well ($\sim$2.18 eV instead 2.202 eV). Hence, in first approximation, the crossing of the index of refraction at the second-harmonic energy with the index at the fundamental frequency will also be at a slightly lower energy. This suggests that the optical properties of our CuCl film can be slightly different from the ones of Haueisens CuCl crystal. At 100 K, the sharp peak is already less sharp and considerable reduced in intensity, and at 200 K (Fig. 6.6) it is not detectable anymore. The increasing phonon activity at higher temperatures quenches this single point of phase matching.

From the literature data summarized in section 6.1, we expect to find the transversal $Z_{3}^{T}$ exciton at 3.203 eV and the transversal $Z_{12}^{T}$ exciton at 3.271 eV, for $T<10$ K. At the lowest temperature the SHG measurements exhibit two second-harmonic resonances: at about 3.18 eV and 3.287 eV. They do not agree exactly with the energies reported in Table 6.1, but from the spike presented above we already saw a slight discrepancy of the optical properties of our sample: this is a CuCl polycrystalline film, whereas most optical measurements are performed on CuCl single crystals, leading to possible shifts in the optical properties. Indeed, CuCl is a strong piezoelectric material and a film (polycrystalline) is more (and differently) subjected to strain and pressure gradients than a single crystal. Yano et al. have studied the
absorption of size dependent CuCl microcrystals in NaCl [12]. They found that at 77 K the $Z_3$ exciton shifts about 30 meV to the blue, when the radii of the CuCl microcrystals decrease from 5.9 nm to 2.1 nm. Similar behaviour can be expected for the $Z_{1,2}$ exciton. This could explain the slightly higher exciton energy we find for the $Z_{1,2}$ exciton, but not the small red shift of the $Z_3$ exciton. Concerning the latter, the second-harmonic data plotted in Fig. 6.5 and Fig. 6.6 are not corrected for interference effects due to the film thickness. The period of the interference is about 115 meV, and could therefore shift one resonance to lower energy, and the other one to higher energy.

Knowing this, we conclude that the energies of the two second-harmonic resonances fit well with the expected single crystal values and we can safely assign the second-harmonic resonances to the $Z_3^T$ and $Z_{1,2}^T$ excitons in the CuCl polycrystalline film. Additional evidence supporting this view is obtained from the line shape of the two second-harmonic resonances, their intensities, and their temperature dependent behaviour, as discussed below.

### 6.3.3 Discussion of exciton characteristics

Cardona established, in first instance from a line shape analysis of the CuCl excitons, that the lowest peak, which shows an extreme sharpness, should be the $Z_3$ exciton and the second (broader) peak the $Z_{1,2}$ exciton [1]. This is opposite to the sequence found in all other Cu halides. Further measurements in CuBr-CuCl mixed compounds supported Cardona’s conclusion. The line width of the $Z_3$-exciton is found experimentally [22] to follow a $T^2$ dependence from 4 to 300 K. This observation may be interpreted [22] as the line width being essentially due to interactions with long-wavelength acoustic phonons. This means that the exciton wave vector $k$ is no longer a good quantum number, implying that in an optical measurement not only the peak at an energy corresponding to $k=0$ is observed, but also states at other $k$ values. If this interpretation is correct, the large $Z_{1,2}$ width is caused by intrinsic effects [2]. The larger number of degenerate scattering states within the $\Gamma_8$ band [2] will give rise to more mixing of different $k$ values, and hence a larger $Z_{1,2}$ width. On the other hand, electrons from the $\Gamma_7$ upper valence band edge can only be scattered into states within the same band [2], and this explains the extreme sharpness of the $Z_3$ exciton in CuCl. For a SHG spectrum we might expect that the line width of the $Z_3$ and $Z_{1,2}$ excitons are comparable to the ones observed in linear optics, since also in a SHG experiment the number of available scattering states and $k$ not being a good quantum number determine the experimental observed exciton line width.

On the contrary, we might expect that the second-harmonic intensity ratio of the $Z_3$ and $Z_{1,2}$ excitons differs from the one found in a linear optical experiment. In a linear optical experiment the line intensity is expected to be proportional to the
number of states available for transitions [1, 2]. This means that the Z_{1,2} exciton has a higher intensity than the Z_3 exciton, which is indeed observed in optical absorption measurements (see Fig. 6.2 and Fig. 6.3). In a SHG experiment, however, during the entire $\omega_{\text{in}} \rightarrow \omega_{\text{in}} \rightarrow 2\omega_{\text{out}}$ cycle the phase needs to be conserved, i.e., the ground state to which the $2\omega$ decays has to be identical to the ground state at the start of the SHG cycle. The second-harmonic intensity, therefore, is proportional to $(N_{\text{coh}})^2$, where $N_{\text{coh}}$ is the number of atoms excited coherently (in phase). Hence, when the exciton $k=0$ state is spread over a large number of states at different energies, because of scattering with acoustic phonons, the number of atoms effectively contributing to the SHG signal at any given energy will be diluted leading to a strong decrease in the second-harmonic intensity. Therefore, contrary to a linear optical experiment, in a second-harmonic experiment the Z_3 exciton is expected to exhibit a higher second-harmonic intensity than the Z_{1,2} exciton. This is in fact what we observe experimentally (see Fig. 6.5).

The temperature dependence of the second-harmonic resonances is shown in Fig. 6.6. At 300 K, no resonance could be detected. Below 200 K, for decreasing temperature a linear increase in intensity of the Z_{1,2} exciton is observed (Fig. 6.6c) in conjunction with a linear shift of the resonance position to lower energies (Fig. 6.6b). Similar behaviour was observed in other optical experiments [29, 36]. In 1963 already, Cardona measured a value of $1.4 \times 10^{-4}$ eV/K for the average temperature coefficient of the energy of the peaks in CuCl, in the range between 4 K and room temperature [1]. Ueta et al. [36] found from their luminescence experiments that the n=1 exciton peak shifts by $2.2 \times 10^{-4}$ eV/K in the temperature range 4 K - 80 K. From the temperature dependent absorption data of Kaifu and Komatsu [22] in the range 10 K - 200 K, a temperature coefficient of $2.5 \times 10^{-4}$ eV/K can be deduced for the Z_{1,2} exciton. The FWM experiments of Kramer and Bloembergen [29] have already been mentioned in section 6.1. They found that the linear temperature dependence of the longitudinal exciton energy between 30 K and 100 K is $2.9 \times 10^{-4}$ eV/K. Our Z_{1,2} exciton energy increases by $2.5 \times 10^{-4}$ eV/K in the temperature range from 20 K to 200 K (Fig. 6.6b). This agrees well with the results of other groups discussed above, confirming the excitonic character of the second-harmonic resonance at 3.3 eV.

In our SHG measurements the Wannier excitons are clearly visible, whereas no second-harmonic intensity enhancement was observed above the conductivity gap. On the other hand, in the SPA (single-photon absorption) and TPA spectroscopic measurements both the Wannier excitons and the conductivity gap are observed with no particular discrimination. In an attempt to understand the difference between the SHG and SPA-TPA spectra, one should look into the differences between these techniques. A major difference is that in SPA and TPA experiments incoherent processes are probed, whereas a SHG experiment involves only coherent processes. To that end, we can give some qualitative arguments concerning our SHG obser-
vations. One should realize that an exciton is a charge-neutral particle, where the electron and hole are bound together, having a single \( k \) vector. Since both particles are always bound to each other, and have a common \( k \) vector, their probability to recombine without losing their \( k \) coherence is much higher than for a free electron and hole, which result from a transition across the conductivity gap. In the latter case the electron and hole are two charged particles moving independently with their own \( k \) vector through the electron-hole continuum. They are, therefore, far more subject to scattering processes and to dephasing, i.e., to lose their \( k \) coherence, than a bound electron-hole pair. Since in a SHG experiment coherence is a prerequisite, a dephased excitation will not contribute to second-harmonic intensity.

In Chapter 2 we also discussed arguments why an exciton should exhibit more SHG than a free electron-hole pair. In the case of CuCl, part of the SHG enhancement at the exciton positions, compared to the conductivity gap, could be due to the microcrystallite structure of the CuCl film, as discussed by Hanamura [8].

In conclusion, we have studied a third kind of excitons, the Wannier excitons, in a temperature-dependent and frequency-dependent SHG experiment. At low temperatures, two second-harmonic resonances were found at about 3.2 eV and 3.3 eV, which we assigned to the \( Z_{3}^{T} \) and \( Z_{1,2}^{T} \) excitons, respectively. The energies, and the temperature dependence of the excitons agree well with earlier reports. However, we did not find any reference which compared the second-harmonic intensity from an exciton with the second-harmonic intensity from interband transitions. The conductivity gap is expected to be observed at about 3.4 eV. Fig. 6.5 shows that no change in the SHG signal is detected in this energy region. We can therefore conclude from our SHG experiments that also Wannier excitons, like Frenkel and charge-transfer excitons, exhibit more second-harmonic intensity than free electron-hole pairs (in other words, interband transitions to the conductivity gap). This implies that SHG is a selective tool for probing and studying excitons, and that interband transitions do not lead to an enhancement in the second-harmonic intensity.

References