Coherent Dynamics of Excitons and Continuum Excitations in Indium Phosphide

by

Gary R. Allan

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Physics
University of Toronto

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Abstract

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A thesis submitted for the degree Doctor of Philosophy
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The dynamics of optically generated, coherent electronic excitations in Indium Phosphide at a temperature of 5 K are investigated over a 140 meV energy range near the band gap using the two-pulse, self-diffracted, degenerate four-wave mixing technique with 30-50 fs near-infra-red pulses and spectrally resolved detection. The coherent dynamics of excitons associated with the fundamental energy gap are investigated under conditions of simultaneous excitation of continuum transitions. Exciton-carrier scattering is shown to produce the dominant source of diffraction for excitons due to excitation-induced dephasing. The dephasing rate of continuum excitations is found to increase abruptly at the threshold energy for LO phonon emission by electrons. Below this threshold energy the dephasing rate is determined to be at least 8 ps$^{-1}$. whereas above the threshold energy, the dephasing rate is at least 13 ps$^{-1}$.

Near the spin-orbit split-off valence to conduction band transition energy the diffracted spectrum is strongly affected by an interaction between split-off excitons and continuum excitations of heavy and light hole bands. A Fano-like spectral profile is observed in the coherent emission spectrum at the split-off transition and the coherent dynamics is dis-
cussed in terms of coupled exciton-continuum excitations. The Fano coupling parameter $q$, which characterizes the spectral profile, is found to decrease as excitation density increases. The interaction matrix element between split-off excitons and continuum excitations is determined to be approximately 5 meV, which corresponds to a 130 fs lifetime over the density range investigated. Observation of the Fano interference phenomenon by four-wave mixing is found to depend on the relative orientation of the electric field polarization vectors. The Fano-like spectral profile is much less prominent for cross-polarized pulses than for co-polarized pulses. Evidence for Fano interference is also observed by spectrally integrated four-wave mixing; there is no evidence of the interference in the cross-polarized case. At present, the polarization dependence is not understood; therefore, the interaction mechanism is not identified but possible interaction mechanisms that could give rise to Fano interference are discussed.
Acknowledgments

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# Contents

Abstract ii

Acknowledgments iv

1 Introduction 1
   1.1 Coherent dynamics and relaxation processes 2
   1.2 Exciton-continuum interactions 6
   1.3 Spectrally resolved four-wave mixing 10
   1.4 Outline of the thesis 12

2 Theory 13
   2.1 Electronic excitations 14
   2.2 Optical Bloch equations 17
      2.2.1 Interactions between electrons and holes 20
   2.3 Two-pulse degenerate FWM 21
      2.3.1 Dependence of FWM on relative polarization of incident pulses 29
   2.4 FWM for interacting excitons and continuum states 32
      2.4.1 Excitation-induced dephasing 33
      2.4.2 Fano resonance at the SO band edge 36

3 Experimental Apparatus 43
   3.1 Laser system 43
      3.1.1 Characterization 47
      3.1.2 Dispersion compensation 48
   3.2 Experimental arrangements 50
   3.3 Sample 54
      3.3.1 Etch procedure 54
      3.3.2 Sample characterization 55
4 Results and Discussion

4.1 General Features .................................................. 59
4.2 Exciton emission due to EID ....................................... 65
4.3 LO phonon emission threshold .................................... 69
4.4 Coherent response at the $E_0 + \Delta_0$ band edge .............. 76

5 Conclusions ............................................................ 96

A Laser Alignment ....................................................... 100
B Electronic Circuits ................................................... 102

References ............................................................... 104
Chapter 1

Introduction

The extensive use of semiconductors in technological applications is largely due to the fact that many electrical properties of semiconductors can be carefully tailored to meet a wide range of requirements. Semiconductors are now used routinely in a wide variety of both electronic and optical devices, such as high-speed transistors, lasers and detectors in telecommunication systems. Tremendous improvements in operating speeds of these devices have allowed the development of telecommunication systems that transmit information at rates in the 10 to 100 gigabit/sec range. In order to utilize fully the enormous bandwidth of optical fibre (which is in excess of 1 terahertz), switching speeds must continue to increase. Understanding the physical processes which determine the electrical properties of semiconductors has contributed to many of the important technological developments that have enabled high speed communication. Over the last 40 years, a great deal has been learned about how electrons interact in semiconductors with a general progression toward understanding processes on faster and faster time scales. As a result of developments in laser technology, it is now possible to investigate electronic interactions on the fastest time scale, i.e. the first interactions that occur after an excitation process. These interactions correspond to coherence decay processes in the context of excitation by coherent laser beams. A thorough understanding of electronic interactions on the fastest time scale may allow the coherent electronic properties of semiconductors to be used in the quest for terahertz switching speeds. In many respects the fundamental limits for switching speeds (using semiconductor based technology) are determined by the electronic response of semiconductors to coherent optical excitation.

This thesis is concerned with measuring the lifetimes of optically generated, coherent electronic excitations in Indium Phosphide (InP) and interpreting the lifetimes in terms of interaction rates for specific processes. InP is particularly suited for investigation of the
coherent response near the spin-orbit split-off valence-to-conduction band transition, which allows electron interactions to be investigated in a different regime than many previous experiments. The results of this thesis are expected to be relevant to other direct gap III-V semiconductors, such as Gallium Arsenide (GaAs) and the In$_x$Ga$_{1-x}$As$_{1-y}$P$_y$ family of alloys.

1.1 Coherent dynamics and relaxation processes

There is great interest in understanding the physical processes that occur during and immediately following optical excitation and there has been considerable effort to develop ultrashort-pulse lasers for investigation of these processes. Over the last three decades, pulse widths have decreased and tuning ranges have increased steadily to the point where coherent optical pulses shorter than 100 femtoseconds ($10^{-13}$ sec) can now be generated over a wide spectral range[1]. Coherent optical radiation interacts with the electronic system of a semiconductor by inducing a time-dependent polarization (charge separation). Optical excitation is the process of energy transfer from the light beam to the electronic polarization and creates a coherent two-particle excitation of an electron and a hole. Experiments with ultrashort pulses have revealed that electronic relaxation can be described microscopically in terms of electrons and holes and generally categorized into three time scales: (i) coherent regime, (ii) cooling regime and (iii) quasi-equilibrium/recombination regime. During the coherent regime, the dynamics of the induced microscopic polarization can be described by a direct phase relationship with the electric field of the optical pulse. The electron and hole dynamics are intimately connected to the dynamics of the polarization. This regime persists until scattering events interrupt the dynamics and destroy the coherent relationship between the polarization and the electric field. Scattering events may also cause the two-particle state to decay into single particle excitations. From this point in time, the electron and hole dynamics are described by the temporal evolution of single-particle distribution functions. During the cooling regime the excited electronic system exchanges energy internally (between electrons and holes) and with the lattice until a thermodynamic quasi-equilibrium, in which the single-particle distribution functions are characterized by the lattice temperature, is established. Relaxation to an unexcited
Chapter 1. Introduction

electronic system occurs by radiative and non-radiative recombination processes during the recombination regime. The time scale for each regime is dependent on material and excitation conditions. e.g. photon energy and pulse intensity, and the regimes overlap to some degree but generally the dynamics proceeds from the coherent regime on the shortest time scale to the recombination regime on long time scales.

The processes which govern the cooling and recombination regimes have been extensively investigated over the past two decades in a variety of materials and for a wide range of excitation conditions[2, 3]. A considerable amount of recent research effort has focussed on the GaAs/AlxGa1-xAs family of bulk and heterostructure materials but other materials, such as InP, Cadmium Sulphide (CdS), and Germanium (Ge), have been investigated too. A fairly comprehensive picture of the cooling and recombination regimes has developed as a result of these efforts. There are two motivations for investigating the coherent regime, which is typically restricted to the first picosecond or less. From a technological point of view, coherent optical excitation may provide access to THz switching rates by circumventing the incoherent relaxation processes that currently limit device speed. Some recent demonstrations of coherently excited electron dynamics are: terahertz frequency radiation emitted from double quantum wells[4], phase control of exciton populations[5] and of photo-currents[6], and Bloch oscillations in super-lattices[7]. The time scale on which these processes can be manipulated is limited to the coherent regime and therefore knowledge of coherence decay times is important for an assessment of the technological merit of these processes. From a fundamental scientific point of view, measuring the rate of decay of coherent states can provide information about the interactions that occur on the fastest time scale following excitation. This information complements the existing body of knowledge obtained from investigations of the cooling and recombination regimes.

The coherence properties of laser beams have been well understood for many years and have been used to investigate coherent excitations of atoms in gases and solid hosts, vibrational and electronic excitations of molecules[8], phonons in solids[9], and, but only recently, electrons in semiconductors[10]. The extremely high dephasing rate typical of electrons in semiconductors prevented observation of many coherent effects until the development of ultrafast lasers. Observing coherent electron dynamics in semiconductors does not merely provide more examples of coherent phenomena that are already well un-
stood (e.g. Rabi flopping, free induction decay, AC Stark effect). The interactions between electrons in a semiconductor can be very strong and provide a fundamental difference compared to atomic systems. The coherent response is not only determined by interactions of electrons with their environment but also by interactions internal to the electronic system. Semiconductors, therefore, are interesting for investigation of coherent properties of a strongly interacting many-body system.

Optical excitation of a semiconductor in the near infra-red or visible range of the spectrum typically corresponds to excitation of an electron across the forbidden energy gap $E_0$, i.e. valence band to conduction band transitions. Fig. 1.1(a) shows a diagram of the band structure of InP in a region that contains the single-particle electron states involved in optical transitions. The optically excited coherent states are superpositions of these single-particle states. There are three valence and one conduction bands and transitions can occur from any valence band to the conduction band. One valence band has a band edge at lower energy than the other two, due to the spin-orbit interaction, and is called the split-off band. The energy separation between the band edges is $\Delta_0$ and there is also a band gap at the energy $E_0 + \Delta_0$. For each valence-to-conduction band transition, the spectrum of excitation is a continuum that has a density of states proportional to the square root of excess energy. Due to the Coulomb interaction between an electron and a hole, absorption also occurs below the band gap energy due to resonances that correspond to bound relative motion of the electron-hole pair: these resonances are called excitons. Fig. 1.1(b) shows a schematic absorption spectrum near the $E_0$ band gap that illustrates the continuum of transitions that exist above $E_0$ and the exciton resonance due to the Coulomb interaction just below $E_0$. In principle there is an exciton resonance associated with each band gap, i.e. each pair of valence and conduction bands. The most widely investigated exciton resonance is associated with the $E_0$ band gap and is referred to as the fundamental exciton. The exciton associated with the $E_0 + \Delta_0$ band gap is referred to as the split-off exciton and has not been investigated by coherent optical spectroscopy in a III-V semiconductor until the work of this thesis.

The scattering processes which lead to the decay of the coherence between the electronic polarization and optical electric field are those that occur on the fastest time scale and can be different for excitons and continuum excitations. In high quality materials at
Figure 1.1: (a) Band structure diagram of InP that illustrates the single-particle states involved in the two-particle coherent excitation process. The bands are labeled as conduction (C), heavy hole (HH), light hole (LH), and spin-orbit split-off (SO) bands and are assumed to be spherically symmetric. The fundamental energy gap is $E_0$ and the spin-orbit splitting energy is $\Delta_0$. (b) Schematic absorption spectrum near $E_0$. The exciton resonance occurs below the band gap energy.
cryogenic temperature, the fundamental exciton dephasing time is typically 1–5 ps whereas continuum dephasing times as short as 14 fs have been reported[11]. The dominant dephasing process is dependent upon excitation conditions, such as exciton or carrier density, and material conditions, such as temperature, impurity density, and disorder. The most important dephasing processes are typically scattering with impurities, defects, phonons, and other carriers (or excitons). A clean separation of these mechanisms is usually not possible but an investigation of the dephasing rate versus energy and density can allow the dominant mechanism(s) to be identified.

1.2 Exciton-continuum interactions

Here the primary motivation for investigating the coherent response of InP above the band gap is described. A context for how these results contribute to the field is also provided. The primary difference between a semiconductor system and an atomic system is the presence of very strong interactions between all electronic excitations in a semiconductor. This is the result of the delocalized nature of electronic excitations in a solid and the relatively long range of the Coulomb interaction compared to typical inter-electron distances. The goal of many major research efforts since the pioneering work of Schultheis et al. [12], who observed the coherent response of fundamental excitons in GaAs, has been to understand the influences of the Coulomb interaction on the coherent response of excitons. Much of the recent research has focussed on excitons associated with the fundamental energy gap in bulk and quantum-well structures because the dephasing time is typically 1 ps and the coherent dynamics can be easily resolved with nominally 100 fs pulses. Indeed, interactions between excitons, which are called many-body effects, have been shown to play an important role[13, 14].

Although many aspects of exciton-exciton interactions are well understood, relatively few experiments have investigated the effects of exciton-continuum interactions on coherent exciton dynamics. Since the work of Schultheis et al. it has been known that the dephasing rate of excitons increases substantially in the presence of free carriers due to scattering of excitons by free carriers (exciton-carrier scattering). Recently experiments have been performed in which populations of excitons and continuum excitations are generated si-
Chapter 1. Introduction

multaneously with the same pulse, which means there is coherence between the exciton and continuum excitations [15, 16, 17, 18, 19, 20, 21]. Under these conditions, the exciton dynamics appear to be significantly different compared to the results of Schultheis et al. obtained with an incoherent free carrier population. Similar observations are reported in this thesis. In some of the reports cited above the different exciton dynamics has been attributed to coherent exciton-continuum coupling, which is only present for simultaneous exciton and continuum excitation. However, it has not been clearly established what the role of incoherent exciton-carrier scattering is in contributing to the difference between the observed dynamics for the two excitation conditions. It appears that a consensus may be emerging[20, 22]; however, a clear explanation of the exciton dynamics observed over a range of excitation density has not been satisfactorily presented. In this thesis, the exciton-continuum interaction is investigated over a wide density range and the observations are discussed in terms of exciton-carrier scattering.

As mentioned, most of the recent research has focussed on exciton dynamics. Comparatively little is known about the dephasing mechanisms of continuum excitations because the dephasing times are typically tens of femtoseconds[11] and are very difficult to resolve temporally. The first measurements of continuum dephasing rates in a semiconductor used pulses of 6 fs duration. Such short pulses have a bandwidth of roughly 200 meV and excite a wide range of transitions. It is not clear that all transitions in this bandwidth should have the same dephasing rate. For instance, at certain energies scattering channels become available that may cause an increase in the dephasing rate above a threshold energy. Examples of such scattering channels are phonon emission and inter-valley transfer within the conduction band. Indeed, more recent experiments have shown that the continuum dephasing rate is affected by additional scattering channels[17, 23]. The dephasing rate may also be different for continuum excitations of the different valence bands. Only a few experiments have investigated continuum dephasing[11, 15, 20, 24, 25] and the dephasing rate was not resolved in all of these reports. Further experiments are needed to examine the energy dependence of continuum dephasing rates.

Another aspect of exciton-continuum interactions is afforded by investigating excitons at higher energy band gaps. In situations where an exciton resonance is degenerate with continuum transitions there is the possibility of observing an effect in the absorption spec-
Chapter 1. Introduction

A spectrum called Fano interference. If an interaction exists between the exciton and degenerate states in a continuum, there is more than one pathway for excitation of the exciton. The absorption spectrum is affected by the interaction because the absorption process must be considered to be a sum over all possible pathways. The amplitudes for various pathways are phase shifted due to the interaction and cause interference in the absorption spectrum, which is typically asymmetric with a distinct minimum on one side of the absorption profile. This effect was first described by Fano for atomic systems[26]. Fig. 1.2 shows an illustration of the energy level diagram and an example absorption spectrum near a Fano resonance. The exciton associated with the split-off band is an example of the degenerate situation required to observe Fano interference. However, these excitons can be difficult to investigate by linear optical spectroscopy because their lifetime can be very short. Other semiconductor systems with suitable energy levels are strained semiconductors, quantum wells, and bulk material in a magnetic field.

The linear optical properties of Fano resonances in semiconductors have been investigated theoretically[27, 28, 29] and experimentally for a variety of systems including quantum wells[30, 31, 32], superlattices[33], and bulk material in a magnetic field[34]. In these systems, some form of confinement is used to establish the required energy degeneracy. Bulk samples provide only a few special cases where a Fano resonance may occur, for example the biexciton, which is analogous to a molecule formed from two excitons, and the split-off exciton. However, for both of these examples decay channels exist that do not result in Fano interference: only decay of the exciton to optically coupled continuum states gives rise to Fano interference. Therefore, the absorption profile may be only very slightly modified due to interference. The linear absorption spectrum of the split-off band edge of GaAs and the biexciton level of CdS do not exhibit clear indications of Fano interference [35, 36]. However, the biexciton level in CdS and CuCl have been shown to exhibit clear Fano interference when investigated by nonlinear spectroscopy[36, 37, 38]. The possibility that this is also true for the split-off exciton has not been investigated until now. In this thesis the split-off exciton is investigated by a nonlinear optical probe, which is described in section 1.3.

Recently, there has been interest in the temporal dynamics of Fano resonances in semiconductors, which is made possible by ultrashort pulse lasers, in the hope that the origin of
Figure 1.2: (a) A schematic energy level diagram of the exciton and continuum two-particle states for two band gaps of a semiconductor. The arrows indicate transition pathways for excitation of the exciton state associated with the higher energy band gap. (b) Absorption spectrum in the presence of an interaction between the lower energy continuum and exciton state (dashed curve) and without any coupling (solid curve). Note: the absorption due to the higher energy continuum is assumed to be very weak.
the interaction may be better understood. However, only a few experiments have examined the temporal dynamics of Fano resonances by nonlinear optical methods[33, 39, 40]. It has been claimed that Fano resonances exhibit temporal characteristics that are very different from the dynamics of fundamental excitons[39, 41]. In fact, the dynamics observed for the Fano resonance were essentially the same as observed for the fundamental exciton under conditions of simultaneous exciton-continuum excitation that was discussed earlier in this chapter. A simple model of a Fano resonance has been shown to be inadequate to explain these observations but no clear explanation has been presented. The split-off exciton provides an example of a Fano resonance different from those previously studied and the possibility of obtaining new insight into the temporal dynamics of Fano resonances in general.

This thesis addresses the nature of the coherent response near the split-off transition of InP, which can be expected to exhibit Fano interference effects. Although GaAs is the most commonly studied direct gap semiconductor for ultrafast research, InP provides a more suitable material for investigations near the split-off transition. In GaAs at the energy resonant with the split-off band edge, carriers injected from the heavy hole band are above the threshold energy for intervalley transfer. Thus it can be difficult to separate effects due to the split-off transition from effects due to intervalley transfer in the conduction band. InP provides a split-off transition that is well below the intervalley scattering threshold energy and, as well, easily accessible with the standard source for ultrashort pulses, which is a mode-locked Titanium-doped sapphire laser. InP is very similar to GaAs in many respects; both are polar, direct-gap semiconductors of the same crystal symmetry class and have similar band structures and effective masses. Therefore many of the same physical processes occur in both materials, which allows many results obtained for GaAs to be applicable to InP.

1.3 Spectrally resolved four-wave mixing

The experimental method used to measure the decay rate of electronic polarization is based on the excite-probe concept. A pulse of light is used to excite a polarization density and a temporally delayed second pulse probes the extent to which the polarization density still
Figure 1.3: Geometry of a four-wave mixing experiment for the purpose of measuring dephasing rates. Two pulses propagating in directions $\vec{K}_1$ and $\vec{K}_2$ excite the sample. The temporal delay between the two excitation pulses is $\tau$ and $c$ is the speed of light. The diffracted power propagating in direction $2\vec{K}_2 - \vec{K}_1$ is measured as a function of delay.

exists when it arrives at the sample. Fig. 1.3 shows an illustration of the experimental geometry, which is called four-wave mixing (FWM). The interaction process is based on interference which can be easily understood if the pulses overlap in time, i.e. for zero delay. The electric fields of the two pulses interfere to form a grating pattern in the optical intensity and hence a grating pattern in the excited carrier density. Since the optical properties of a semiconductor are affected by an excited carrier density, the grating causes diffraction of light. For temporally separated pulses, interference occurs between the electric field of the second pulse and the polarization density excited by the first pulse to create a population grating that causes diffraction of some light from the second pulse. A measurement of the diffracted power as a function of delay time can give direct insight into the polarization lifetime\cite{42}. This technique allows a measurement of the dephasing rate even for inhomogeneously broadened systems because the multiple pulse interaction probes the polarization dynamics microscopically. The diffraction process can be considered as an interaction between two electric fields that write a grating and a third electric field that diffracts from the grating. In this sense, FWM can be considered a third-order nonlinear
optical response (a $\chi^{(3)}$ nonlinearity).

The temporal resolution of the FWM geometry is defined by the pulse width. Resolving the dephasing rate of continuum excitations requires pulses with durations in the range 10–50 femtoseconds. Lasers with pulse widths this short are state-of-the-art and are not available commercially. Construction of a laser system that provides 30–50 femtosecond tunable pulses was a major part of this thesis work. These ultrashort optical pulses have such a large bandwidth that the concept of tunable spectroscopy is rather poorly defined. In order to investigate the energy dependence of dephasing processes, the diffracted beam is spectrally resolved. The power spectrum is interpreted as the spectral distribution of coherent excitations that have not depolarized during the delay time. In this way spectroscopic information can be obtained on an energy scale smaller than the pulse bandwidth.

1.4 Outline of the thesis

A detailed theoretical description of the diffraction process is presented in Chapter 2. This theory provides a framework for the interpretation of the experimental results. Some illustrative examples are presented for simplified systems to explain the fundamental processes. The apparatus and techniques used to perform the experiments are discussed in Chapter 3. The laser system, which made the measurements possible, is described in detail. The experimental results are presented and discussed in Chapter 4 in three sections. An investigation of the fundamental exciton dynamics under conditions of strong exciton-continuum coupling is presented first. In the last two sections, the response of the continuum is investigated near the band edge and near the spin-orbit split-off transition. A summary of the results and a discussion of related future work is presented in Chapter 5.
Chapter 2

Theory

A simple theory of the electronic response of a semiconductor to coherent optical radiation is presented in this chapter for the purpose of interpreting FWM experiments described in this thesis. A complete description of coherent electron dynamics in a semiconductor is very complicated because of the strong interactions that exist between electrons: a many-body description is required. In addition, the strength of the Coulomb interaction between electrons is a function of the excited electron density due to screening. The approach taken in this thesis is to employ as simple a theory as possible for the purpose of analyzing the FWM experiments. The simplest description of coherent dynamics is given by the optical Bloch equations (OBE) for a two-level system. An appropriate model for the continuum excitations of a semiconductor is a collection of two-level systems with a distribution of energies. However for the conditions of the experiments performed for this thesis, the optical Bloch equations must be modified to model the coherent dynamics of excitons. The extensions that are required are described in this chapter. In the first section, the exciton and continuum excitations that are involved in the experiments are defined. To illustrate some fundamental concepts, the dynamics of a two-level system as given by the OBE is reviewed. The complications introduced by interactions between electrons are then discussed and it is shown that the OBE are valid for both excitons and continuum excitations in the non-interacting limit. Illustrative examples of a FWM experiment are presented for both excitons and continuum excitations in the non-interacting limit, to point out the essential differences between the FWM signals for these two types of systems. The extensions to the OBE required to include exciton-continuum interactions are discussed for two specific cases. The first case pertains to excitation of the fundamental exciton simultaneously with a large bandwidth of continuum excitations. An additional source of diffraction for excitons is shown to result from exciton-continuum interactions; this
diffraction mechanism is referred to as excitation-induced dephasing. The second case is relevant to an exciton that is coupled to an energetically degenerate continuum of states, which is the required type of system to observe Fano interference effects. The exciton-continuum interaction is treated phenomenologically in both cases.

2.1 Electronic excitations

The electronic states that can be optically excited with a photon energy comparable to the fundamental band gap energy are the states in the highest energy valence bands and the lowest energy conduction band. A portion of the electronic band structure of InP near the center of the Brillouin zone is shown in Fig. 2.1(a). There are one conduction (C) and three valence bands, which are called the heavy hole (HH), light hole (LH), and split-off hole (SO) bands. For simplicity the bands are assumed to be spherical in k-space. The band gap energy is denoted $E_0$ and the spin-orbit splitting energy is denoted $\Delta_0$. The important energies and band parameters are tabulated in Table 2.1.

Above $E_0$ the optical absorption spectrum corresponds to a continuum of valence to conduction band transitions that create an electron in the conduction band and a hole in the valence band. The states involved in these two-particle excitations are depicted in Fig. 2.1(a) by the vertical arrows. This thesis is concerned with coherent states of an electron-hole pair that are excited by coherent optical radiation. Due to the Coulomb interaction between an electron and a hole, absorption resonances occur below $E_0$ that correspond to bound states of the Coulomb potential, i.e. bound electron-hole relative motion. These resonances are called excitons and have a binding energy $E_b$ of 5 meV. The continuum of excitations corresponds to the unbound states of the Coulomb potential and can also be called excitons. In order to be able to refer to these two types of excitations without ambiguity, the unbound states are called continuum excitations. The name free carrier transitions is also used in the literature but in this thesis free carrier is used to refer to the single-particle states. Fig. 2.1(b) shows the excitation spectrum in the "exciton" picture. There are exciton and continuum excitations associated with each pair of bands. The levels for each pair are separated for clarity but the horizontal axis has no physical meaning. The HH and LH excitons are referred to jointly as the fundamental exciton.
Figure 2.1: (a) Schematic band structure diagram of InP. The energy axis is not to scale in order to show the valence bands more clearly. Optical excitation processes at a photon energy near $E_0 + \Delta_0$ are depicted by the vertical arrows. (b) Energy level diagram of the excitation spectrum in the exciton picture.
Chapter 2. Theory

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Table 2.1: Parameters are for lattice temperature of 4 K and obtained from Reference [43]. The unit for the effective masses is the mass of an electron, \( m_0 \). Phonon energies correspond to phonons at the center of the Brillouin zone.

The continuum absorption spectrum below \( E_0 + \Delta_0 \) is comprised of both HH and LH transitions but the HH transitions provide the dominant contribution to the absorption (approximately in the ratio 2:1) because of the larger effective mass of the HH band. Above \( E_0 + \Delta_0 \) the continuum spectrum is also dominated by HH transitions because the density of states (which is proportional to the square root of excess energy for parabolic band dispersion) of the SO band is small near the band edge.
2.2 Optical Bloch equations

In this section, a semiclassical model of the interaction between coherent radiation and a two-level system is reviewed [44]. First the concept of polarization is defined quantum mechanically and then a notation for the density matrix formalism is defined. The temporal dynamics of a two-level system subject to pulsed optical excitation is discussed and applied to an ensemble of systems.

A valence band state and a conduction band state with the same wave vector, \( k \), form a two-level system for an electron (the direction of the wave vector is not important in this section). The states are denoted \( |v, k\rangle \) and \( |c, k\rangle \) and have energies \( \varepsilon_v(k) \) and \( \varepsilon_c(k) \). The electric field of coherent radiation interacts with a semiconductor by inducing a polarization. The semiclassical interpretation of this interaction process is that the electron wavefunction \( \psi_k \) evolves in time under the influence of a classical electric field \( E(t) \). The temporal dynamics of \( \psi_k \) is given by Schrödinger’s equation, which is

\[
\frac{i\hbar}{\partial t} |\psi_k\rangle = H |\psi_k\rangle
\]

(2.1)

where \( H \) is the Hamiltonian operator. The interaction Hamiltonian in the electric dipole approximation is \(-\vec{\mu} \cdot E(t)\), where \( \vec{\mu} \) is the dipole moment, and is treated as a perturbation of the bare Hamiltonian. The dipole moment is assumed to have non-zero off-diagonal (interband) matrix elements, \( \vec{\mu}_{cv} = \langle c, k | \vec{\mu} | v, k \rangle \), and to have \( \vec{\mu}_{cc} = \vec{\mu}_{vv} = 0 \). The electric field is written as a product of a slowly varying amplitude \( \tilde{E}(t) \) and a carrier wave with frequency \( \omega_0 \):

\[
E(t) = \tilde{E}(t)(e^{i\omega_0 t} + e^{-i\omega_0 t}).
\]

(2.2)

If the system is initially in state \( |v, k\rangle \), optical excitation causes transitions to occur from \( |v, k\rangle \) to \( |c, k\rangle \); however, the transition process is not instantaneous. The dynamics of \( |\psi_k\rangle \), as determined by Eq. 2.1, can be interpreted in terms of a time-dependent superposition of basis states.

\[
\psi_k(t) = a_{c,k}(t)|c, k\rangle + a_{v,k}(t)|v, k\rangle
\]

(2.3)

with temporally varying amplitudes, \( a_{c,k}(t) \) and \( a_{v,k}(t) \), such that the expectation value of the dipole moment,

\[
\langle \psi_k | \vec{\mu} | \psi_k \rangle = 2 \text{Re}[a_{c,k}^*(t)a_{v,k}(t)\vec{\mu}_{cv}]
\]

(2.4)
oscillates at $\omega_0$. The electronic interband polarization is defined as the dimensionless quantity $a^*_c a_{v,k}$. The probability that the electron is in state $|c, k\rangle$ ($|v, k\rangle$) is $|a^*_c|^2 (|a_{v,k}|^2)$. which is defined as the occupation of state $|c, k\rangle$ ($|v, k\rangle$). In this two-level system model, the polarization magnitude (but not its phase) is completely determined by the occupations for all time, which constitutes the regime of coherent dynamics.

However, relaxation processes will eventually bring an ensemble of systems into thermal equilibrium, which in general cannot be described by a wavefunction since the ensemble can have a non-zero upper state occupation and zero polarization magnitude. A density matrix is used to describe the statistical properties of a distribution of ensembles that can each be described by a wavefunction. The density matrix is defined as

$$\rho = \sum_k \rho_k = \sum_k C_k |\psi_k\rangle\langle\psi_k|$$  \hspace{1cm} (2.3)

where $C_k$ is the fraction of systems in state $|\psi_k\rangle$. In the density matrix formalism, the occupations and the polarization for each system labeled by $k$ are treated as separate variables that are coupled by an electric field. The notation for the density matrix is:

$$\rho_k = \begin{bmatrix} f_{v,k} & P_k e^{-i\omega_0 t} \\ P_k^* e^{i\omega_0 t} & f_{c,k} \end{bmatrix}$$  \hspace{1cm} (2.6)

where $P_k$ is the slowly varying amplitude of the polarization, while $f_{c,k}$ and $f_{v,k}$ are the occupations of the conduction and valence band states. The electron-hole representation is used by making the following substitutions: $f_{c,k} \rightarrow f_{c,k}$ and $f_{v,k} \rightarrow 1 - f_{h,k}$.

The equation of motion of $\rho_k$ is determined by the Liouville equation, which is

$$i\hbar \frac{\partial}{\partial t} \rho_k = [\rho_k, -\vec{\mu} \cdot \vec{E}(t) + H_{\text{relax}}]$$  \hspace{1cm} (2.7)

where $H_{\text{relax}}$ is the relaxation Hamiltonian that accounts for external interactions. The temporal evolution of $\rho_k$ due to $-\vec{\mu} \cdot \vec{E}(t)$ is called coherent dynamics whereas $H_{\text{relax}}$ determines the incoherent dynamics. A polarization decay rate that is greater than the occupation decay rate implies a transition from a pure to a mixed state on a timescale of the polarization decay time. Relaxation processes are referred to as incoherent scattering processes. Rate equations for the polarization and occupations under the influence of a driving electric field can be derived from Eq. 2.7 by making the rotating wave approximation[44, 45].
and the set of equations obtained is referred to as the optical Bloch equations (OBE). With the coherent parts written explicitly the OBE are:

\[
\left( \frac{\partial}{\partial t} + i \nu_k \right) P_k = i(1 - 2f_k)\Omega + \frac{\partial P_k}{\partial t}_{\text{incoh}} \tag{2.8}
\]

\[
\frac{\partial}{\partial t} f_k = -i [\Omega^* P_k - \Omega P_k^*] + \frac{\partial f_k}{\partial t}_{\text{incoh}} \tag{2.9}
\]

where \( \Omega = \mu_{ee} \tilde{E}(t)/\hbar \) is the Rabi frequency and \( \nu_k = \varepsilon_c(k) - \varepsilon_v(k) - \omega_0 \) is the detuning. The dynamics of \( f_{e,k} \) and \( f_{h,k} \) are identical in the two-level system and \( f_k \) refers to both. A Boltzmann approximation is used for the incoherent scattering terms, which are assumed to be proportional to phenomenological decay rates, \( \gamma_k \) for the polarization and \( \gamma_{\text{recomb}} \) for the occupations. The decay terms are

\[
\frac{\partial P_k}{\partial t}_{\text{incoh}} = -\gamma_k P_k \tag{2.10}
\]

\[
\frac{\partial f_k}{\partial t}_{\text{incoh}} = -\gamma_{\text{recomb}} f_k \tag{2.11}
\]

where \( \gamma_k \) and \( \gamma_{\text{recomb}} \) are the inverses of the transverse \( (T_2) \) and longitudinal \( (T_1) \) time constants commonly defined for atomic systems. With the decay terms written explicitly, the OBE are:

\[
\left( \frac{\partial}{\partial t} + i \nu_k + \gamma_k \right) P_k = i(1 - 2f_k)\Omega \tag{2.12}
\]

\[
\left( \frac{\partial}{\partial t} + \gamma_{\text{recomb}} \right) f_k = -i [\Omega^* P_k - \Omega P_k^*] \tag{2.13}
\]

The physics of the interaction of the two-level system with the electric field is readily apparent from the OBE. The electric field drives the polarization, which oscillates at the carrier frequency but is phase shifted by an amount determined by \( \nu_k \) (a \( \pi/2 \) phase shift results on resonance). The polarization interacts with the electric field to drive the occupation (strongest driving occurs on resonance). A non-zero occupation reduces the effective strength of the electric field due to saturation. If the electric field is switched off, the polarization continues to oscillate but at its resonant frequency (as opposed to \( \omega_0 \)) and decays exponentially at a rate \( \gamma_k \). The occupation does not oscillate but simply decays at a rate \( \gamma_{\text{recomb}} \).
2.2.1 Interactions between electrons and holes

The dynamics of a two-level system described by the OBE only account for interactions between electrons that lead to incoherent scattering. However, the Coulomb potential can also cause coherent interactions between electrons and holes. The excitation spectrum of a semiconductor has been discussed in terms of excitons and continuum excitations, which are the bound and unbound states of the potential formed by the Coulomb interaction between an electron and a hole. In this sense, the dominant effect of the Coulomb interaction is the formation of exciton resonances, which are electron-hole pair states. The long range of the Coulomb potential can also cause interactions between electron-hole pairs. For example, the electric field associated with the polarization of an electron-hole pair is experienced by other electron-hole pairs. Several four-wave mixing (FWM) experiments have demonstrated the strong influence of the Coulomb interaction on the coherent response of excitons[13, 14, 46, 47, 48, 49]. Effects related to interactions between electrons (and holes) are called many-body effects and are not explicitly included in the OBE.

There have been many efforts to derive equations for the dynamic coherent response of a semiconductor that include many-body effects[50, 51, 52, 53]. For the Coulomb interaction the equations so derived are extremely complicated. Tractable equations can only be obtained by making certain approximations. The standard approach is to use a two-band model and a basis of single-particle states that are coupled by the Coulomb interaction. The basis states are labeled by the wave vector, $k$ (the explicit vector notation is suppressed). The Coulomb matrix element between two states $k$ and $k'$ in a volume $L^3$ is a function of the magnitude of the wave vector exchanged in the scattering process, $s$, and is given by the following expression if the effects of screening are ignored:

$$V(s) = \frac{e^2}{L^3 \varepsilon_{\infty}} \frac{1}{s^2}. \quad (2.14)$$

The dynamics of the polarizations and occupations are obtained by the same method as outlined for the OBE but the Coulomb interaction introduces a coupling between all states. The random phase approximation leads to a set of coupled equations called the semiconductor Bloch equations (SBE)[52, 54, 55]. The SBE are presented here but are not derived. The SBE have the form of the OBE but the Rabi frequency and detuning are redefined. The incoherent scattering rates for the polarization and occupation can be
defined in terms of the Coulomb interaction, although approximations need to be made to obtain simple expressions[52]. Additional phenomenological decay rates need only to be introduced to account for other interactions. With a Boltzmann approximation for the incoherent scattering terms (as used for the OBE), the SBE are:

$$\left( \frac{\partial}{\partial t} + i \tilde{\nu}_k + \gamma_k \right) P_k = i(1 - 2f_k) \tilde{\Omega} \tag{2.15}$$

$$\left( \frac{\partial}{\partial t} + \gamma_{k,\text{scatt}} \right) f_k = -i \left[ \tilde{\Omega}^* P_k - \tilde{\Omega} P_k^* \right]. \tag{2.16}$$

where

$$\tilde{\Omega} = \frac{\mu_{ee} \tilde{E}(t)}{\hbar} + \sum_{k'} \frac{V(k - k')}{\hbar} P_{k'} \tag{2.17}$$

$$\tilde{\nu}_k = \varepsilon_e(k) - \varepsilon_v(k) - \omega_0 - 2 \sum_{k'} \frac{V(k - k')}{\hbar} f_{k'} \tag{2.18}$$

The SBE can be solved analytically, in the low density limit, if the dephasing rate is assumed to be zero. The result is an uncoupled set of equations that have the same form as the OBE but represent an excitation spectrum of excitons and continuum excitations[45]. Thus the equations describing the coherent dynamics of excitons and continuum excitations in the non-interacting limit can be derived from the SBE if $f_k$ is set to zero in Eq. 2.18. i.e. only the correction to $\Omega$ is retained, which is valid in the low density limit. When the OBE are applied to a system of excitons or continuum excitations the label $k$ is taken to refer to the energy of the electron-hole pair state.

### 2.3 Two-pulse degenerate FWM

Many of the results of this thesis can be interpreted as the dynamics of a distribution of excitons and/or continuum excitations distributed in space and distinguished by the label $k$. In this section, the dynamics of non-interacting distributions of excitons and continuum excitations are discussed separately to illustrate the basic physical processes involved in a FWM experiment. The main difference between these two systems is the distribution of resonant energies; all excitons are assumed to have the same energy (a homogeneously broadened ensemble) whereas the continuum states are assumed to have an energy dispersion that is quadratic in the label $k$ (an inhomogeneously broadened ensemble).
Figure 2.2: Schematic diagram of the experimental geometry of a FWM experiment. The speed of light is $c$ and $\tau$ is the temporal delay between pulses.

The FWM experimental geometry used for this thesis is schematically illustrated in Fig. 2.2. A pulse with propagation vector $\vec{K}_1$ excites the sample at a time $t = -\tau$ and a second pulse with propagation vector $\vec{K}_2$ arrives at time $t = 0$. The electric field of the second pulse interferes with the polarization density created by the first pulse to form a population grating with wave vector $\vec{K}_1 - \vec{K}_2$. The population affects the index of refraction of the material and therefore the second pulse experiences a grating of the optical properties, which causes some light to be diffracted into the direction $2\vec{K}_2 - \vec{K}_1$. The physical quantity measured in the FWM experiments is the radiation emitted by the macroscopic polarization density, $P(t)$, into the direction $2\vec{K}_2 - \vec{K}_1$ as a function of delay and is a direct probe of the electronic coherence in the sample. The terms diffraction and emission are used interchangeably throughout this thesis, although emission more accurately conveys the correct physical picture. The temporal profile of $P(t)$ is obtained by summing over the contributions of each state:

$$P(t) = \text{trace}(\rho\mu) = \sum_k \left( P_k e^{-i\omega_0 t} \mu_{cv}^* + P_k^* e^{i\omega_0 t} \mu_{cv} \right)$$

(2.19)

The OBE pertain to a spatially homogeneous electric field but the excitation conditions
are spatially inhomogeneous, since
\[ \tilde{E}(t) = \tilde{E}_1(t + \tau)e^{i\tilde{K}_1 \cdot \tilde{r}} + \tilde{E}_2(t)e^{i\tilde{K}_2 \cdot \tilde{r}}. \] (2.20)

As long as the length scale of the spatial inhomogeneity is much larger than the length scale of the wavefunction for an electron-hole pair (approximately the exciton Bohr radius), homogeneous conditions can be applied to the small region of space occupied by an electron-hole pair. This condition is satisfied for the experiments discussed here, since the angle between \( \tilde{K}_1 \) and \( \tilde{K}_2 \) is approximately \( 1^\circ \). Therefore, \( P_k \) and \( f_k \) can be considered to be slowly varying functions of spatial co-ordinates. The periodicity of the inhomogeneity allows the OBE to be solved for spatial Fourier amplitudes of \( P_k(\tilde{r}) \) and \( f_k(\tilde{r}) \). A convenient basis for the spatial Fourier series of \( P_k(\tilde{r}) \) is the set of plane waves propagating in the diffraction directions for the geometry shown in Fig. 2.2. For \( f_k(\tilde{r}) \) the convenient basis is the set of plane waves with propagation vectors given by harmonics of the grating wave vector plus a spatially homogeneous component. In terms of the vectors \( \tilde{K} \) and \( \tilde{Q} \), which are defined as (see Fig. 2.2)

\[ \tilde{K} = \frac{1}{2}(\tilde{K}_1 + \tilde{K}_2) \]  
\[ \tilde{Q} = \frac{1}{2}(\tilde{K}_1 - \tilde{K}_2). \] (2.21) (2.22)

the spatial Fourier series for the polarization, occupation, and Rabi frequency are

\[ P_k(\tilde{r}, t) = \sum_{n = -\infty}^{\infty} P^{(2n+1)}_k(t) e^{i(\tilde{K}+(2n+1)\tilde{Q}) \cdot \tilde{r}} \] (2.23)

\[ f_k(\tilde{r}, t) = \sum_{m = -\infty}^{\infty} f^{(2m)}_k(t) e^{i2m\tilde{Q} \cdot \tilde{r}} \] (2.24)

\[ \Omega(\tilde{r}, t) = \Omega^{(1)}(t) e^{i(\tilde{K}+\tilde{Q}) \cdot \tilde{r}} + \Omega^{(-1)}(t) e^{i(\tilde{K}-\tilde{Q}) \cdot \tilde{r}}. \] (2.25)

The temporal dynamics of each component can be obtained by substituting the Fourier series (Eqs. 2.23–2.25) into the OBE. The source for radiation emitted into the direction \( 2\tilde{K}_2 - \tilde{K}_1 \) corresponds to \( \sum_k P_k^{(-3)} \). In the small signal limit, the expansions can be truncated and only \( f^{(0)}_k, f^{(2)}_k, P^{(1)}_k, P^{(3)}_k \) need to be calculated[55]. This truncation corresponds to a perturbation approach and is referred to as the \( \chi^{(3)} \) limit in the language of nonlinear optics[56]. The rate equations required to obtain the diffraction component.
Eq. 2.30 shows that the source for the FWM signal is the optical electric field that diffracts from the occupation grating represented by \( f_k^{(-2)} \).

The difference in energy distributions for excitons and continuum excitations has a profound effect on the temporal characteristics of the diffracted pulse in a FWM experiment. As mentioned previously, the excitons are all assumed to have the same energy whereas the continuum excitations have different energies. As an illustration of the effect of this difference, the temporal evolution of the diffracted intensity is depicted in Fig. 2.3 for both cases. In Fig. 2.3(a), the temporal profile and timing of the excitation pulses are shown (second pulse arrives at \( t=0 \)). After excitation of excitons by the first pulse, the dynamics of \( P(t) \) is governed by the decay of coherence and is called free induction decay (FID). The second pulse interferes with \( P(t) \) to form a population grating that leads to coherent emission in the diffraction direction. The temporal profile of the diffracted intensity is shown in Fig. 2.3(b).

For excitation of the continuum states, \( P(t) \) decays on a timescale determined by the bandwidth of excitation, since each \( P_k \) oscillates at its resonant frequency after the electric field is turned off. However, \( P_k \) decays exponentially at the dephasing rate and, therefore, the electric field of the second pulse, \( \tilde{E}_2(t) \), interferes with each \( P_k \) to create an occupation grating (described by \( f_k^{(\pm 2)} \)) for each energy ensemble. There is a phase difference between \( P_k \) and \( \tilde{E}_2(t) \) that is a function of \( k \), because the polarizations evolve at their resonant frequencies (\( \nu_k \)) during the interval between pulses. This temporal phase shift manifests as a spatial phase shift for \( f_k^{(\pm 2)} \) that is a function of \( k \). For delays greater than the pulse width, the phase shifts cause the total population to be spatially homogeneous (i.e.
Figure 2.3: An illustration of the temporal profile of the diffracted emission in a FWM experiment for both exciton and continuum states. In (a) is shown the excitation pulse sequence. The temporal profile of the diffracted signal from (b) a system of excitons is free induction decay and from (c) a system of continuum excitations is a photon echo.
no grating). However, the electric field of the second pulse interacts with each $f_k^{(-2)}$ to produce a diffracting polarization component ($P_k^{(-3)}$) at each energy. The spatial phase shifts of the gratings cause the diffracting polarizations to be phase shifted across the distribution. The phase shift as a function of energy is an increasing lag for higher energy. Since the polarizations evolve in time at their resonant frequencies after the second pulse is gone, the distribution of polarizations rephases at a time equal to the delay interval to form a macroscopic polarization density that radiates into the FWM direction. This emission is called a photon echo and is depicted in Fig. 2.3(c).

FWM experiments were performed with both spectrally integrated and spectrally resolved detection. The predictions of the OBE for the coherent response of excitons and continuum states are discussed for both types of measurements. In spectrally integrated FWM the energy in the diffracted pulse,

$$J(\tau) \propto \int_{-\infty}^{\infty} \left| \sum_k \mu_{\nu k}^* P_k^{(-3)}(t) \right|^2 dt$$

(2.31)

is measured as a function of delay to determine the dephasing rate. In the limit of delta function optical pulses, the OBE can be solved analytically. The result for continuum excitations is that $J(\tau)$ decays exponentially as a function of delay with a time constant $\tau_{echo} = \frac{1}{4} \gamma_k$, if the dephasing rate is not a function of $k$. For excitons the time constant is $T_{FID} = \frac{1}{2} \gamma_e$. However, the delta function approximation is usually not valid for continuum excitations because the continuum dephasing rate is typically comparable to the pulse bandwidth. The resolution limit for the decay constant is primarily determined by the noise floor and can be less than half the pulse width. If the profile of $J(\tau)$ is affected by convolution with the pulse profile, the OBE must be integrated numerically to account for the convolution. A series of calculations were performed and the results were compared to experimental data for the purpose of understanding the extent to which the decay of $J(\tau)$ is affected by the pulse profile. However, the usefulness of this procedure is limited by the extent to which the pulse temporal profile is characterized. Knowledge of the pulse profile is usually inadequate to extract dephasing times that are comparable to the pulse width[57].
In spectrally resolved FWM the power spectrum of the diffracted pulse,

\[ S(\omega_s, \tau) \propto \left| \int_{-\infty}^{\infty} \sum_k \mu_k^* P_k^{(-3)}(t) e^{i\omega_s t} dt \right|^2 \]  \hspace{1cm} (2.32)

is measured as a function of delay to determine if \( \gamma_k \) is a function of energy. The FWM spectrum can be interpreted as the spectrum of excitations that have not yet dephased after a time \( \tau \). A variation of the dephasing rate with energy can be detected in this way. However, \( S(\omega_s, \tau) \) can be affected by interference which stems from the fact that \( P(t) \) is not exactly the Fourier transform of the spectrum of coherent continuum excitations. Since each \( P_k^{(-3)} \) component decays with time, there is a spectral width associated with the emission from each component that can overlap the emission spectrum from other components\[57, 58\]. The interference develops as delay increases and can be important for the continuum states because the dephasing rates are very high and therefore the energy range over which interference can occur is large. A calculation of \( S(\omega_s, \tau) \) using the OBE was performed with 1000 points in \( k \)-space from zero to 500 \( \mu m^{-1} \) over a temporal range of 1.2 ps with a 1.2 fs step size. The results of the calculation are shown in Fig. 2.4 with the parameters listed in the caption. Although a constant dephasing rate was used, the spectrum appears to decay faster at the extremes (circles) than at the peak of the excitation (solid curve). This is the result of interferences that develop as delay increases. Therefore, decay constants should only be extracted from spectrally integrated data.
Figure 2.4: An example of the spectrally resolved FWM signal calculated with the OBE. The parameters were: photon energy $\hbar \omega_0 = 1.46$ eV, 50 fs pulse width, and 10 ps$^{-1}$ dephasing rate. Results are shown for five energies, $\hbar \omega_s$, relative to the peak of the laser spectrum: 0 meV (solid line); +10 meV (solid square), -10 meV (hollow square), +20 meV (solid circle), -20 meV (hollow circle).
2.3.1 Dependence of FWM on relative polarization of incident pulses

The two-level model is inadequate to describe the FWM process in semiconductors if the optical pulses do not have the same polarization. A model system with at least three-levels (one ground state and two excited states), where the transitions to each excited state have different dipole matrix elements, is required [59, 60, 61, 62]. The coupling efficiency of optical radiation to an electronic transition is determined by the projection of the electric field vector onto the dipole moment. Therefore, the symmetry of the dipole moment matrix elements determine the optical absorption selection rules of the crystal. In this section, the FWM diffraction mechanism is analyzed for parallel and perpendicular linearly polarized pulses because FWM experiments were performed for both configurations. The two configurations are denoted as \( xx \) and \( xy \).

The dipole moments of the interband transitions for InP as determined by the crystal symmetry and ignoring the \( k \)-dependence of the Bloch states are tabulated in Table 2.2 [63]. The states are the single-particle states and are labeled by band and by the projection of the total angular momentum \( \vec{J}_k \) (orbital plus spin) onto the direction of the electron wave vector. Coherent electron-hole pair states have a polarization direction determined by the direction of the electric field. The dipole matrix elements in Table 2.2 can be used to determine which single-particle states make up an electron-hole pair state with a particular polarization direction, i.e. determine the selection rules for excitons. The quantization direction for the angular momentum of electron-hole pair states \( \vec{J}_X \) is chosen to be the average propagation direction of the laser beams, \( \vec{K} \), which is nearly equal to both propagation directions \( \vec{K}_1 \) and \( \vec{K}_2 \) since the angle between the beams is small. The total angular momentum of the optically active electron-hole pair states is \( J_X = 1 \), since the ground state has \( J_X = 0 \) \( (\Delta J_X = 0.2 \) transitions are not allowed in the electric dipole approximation). The exciton (or continuum) basis states of angular momentum are labeled by the projection of \( \vec{J}_X \) on the quantization direction as \(|X, 0 \rangle, |X, + \rangle \) and \(|X, - \rangle \) for \( m_X = 0, +1, -1 \) respectively. There is no electric field along the propagation direction in either \( xx \) or \( xy \) configuration and therefore the \(|X, 0 \rangle \) state is not optically excited. Basis vectors for right and left circular polarizations are denoted by \( \hat{\sigma}_+ \) and \( \hat{\sigma}_- \), respectively, and
<table>
<thead>
<tr>
<th>band</th>
<th>$m_J$</th>
<th>$C + 1/2$</th>
<th>$C - 1/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH</td>
<td>+3/2</td>
<td>$(\lambda + i\beta)/\sqrt{2}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>-3/2</td>
<td>0</td>
<td>$(\lambda - i\beta)/\sqrt{2}$</td>
</tr>
<tr>
<td>LH</td>
<td>+1/2</td>
<td>$-\sqrt{2/3}\nu$</td>
<td>$(\lambda + i\beta)/\sqrt{6}$</td>
</tr>
<tr>
<td></td>
<td>-1/2</td>
<td>$-\lambda + i\beta)/\sqrt{6}$</td>
<td>$-\sqrt{2/3}\nu$</td>
</tr>
<tr>
<td>SO</td>
<td>+1/2</td>
<td>$\nu/\sqrt{3}$</td>
<td>$(\lambda + i\beta)/3$</td>
</tr>
<tr>
<td></td>
<td>-1/2</td>
<td>$-\lambda + i\beta)/\sqrt{3}$</td>
<td>$\nu/\sqrt{3}$</td>
</tr>
</tbody>
</table>

Table 2.2: Dipole matrix element for optical transitions from the valence to conduction bands with $\vec{k} = 0$ Bloch states. The vectors $(\nu, \lambda, \beta)$ form an orthogonal basis with $\nu$ parallel to the electron wave vector, $\vec{k}$. The quantization direction is along the wave vector $\vec{k}$ in this basis.

Vectors for linear polarizations are denoted by \( \hat{x} = \frac{1}{2}(\hat{\sigma}_+ + \hat{\sigma}_-) \) and \( \hat{y} = \frac{1}{2}(\hat{\sigma}_+ - \hat{\sigma}_-) \).

In an exciton basis, the optically excited states are polarized in the direction of the electric field. The exciton wavefunction is therefore a superposition of the basis states:

\[
|X\rangle = a_0|0\rangle + a_+|X. +\rangle + a_-|X. -\rangle
\]  

(2.33)

where $|0\rangle$ represents the ground state. The density matrix of the three-level system is

\[
\rho = \begin{bmatrix}
N_0 & P_+ & P_- \\
P_+^* & N_+ & 0 \\
P_-^* & 0 & N_- \\
\end{bmatrix}
\]  

(2.34)

where $N_0$, $N_+$ and $N_-$ are the occupations of $|0\rangle$, $|X. +\rangle$ and $|X. -\rangle$ respectively, while $P_+$ and $P_-$ are the polarizations of the pairs $|0\rangle, |X. +\rangle$ and $|0\rangle, |X. -\rangle$, respectively. The temporal evolution of the matrix elements of $\rho$ can be calculated in the same way as was done for the two-level model but the total polarization density is given by

\[
\vec{P} = \sum_k (P_+ \mu^* + P_- \mu^* \mu) \hat{\sigma}_+ + (P_- \mu \mu^* + P_- \mu^* \mu) \hat{\sigma}_-
\]  

(2.35)

where the magnitude of the dipole moment matrix elements are assumed to be the same for both transitions. The diffraction components of the polarization density can be obtained
by solving the system of equations 2.26–2.30 with Dirac delta function excitation pulses. 
i.e. \( \vec{E}^{(1)} = \vec{A}_1 \delta(t + \tau) \) and \( \vec{E}^{(-1)} = \vec{A}_2 \delta(t) \). The results are [60, 64, 22]

\[
P_+^{(-3)}(t) = -2i\mu^3(\sigma_+ \cdot \vec{A}_2)(\sigma_+ \cdot \vec{A}_1)^*(e^{i\omega_k t - \gamma t} \Theta(t - \tau) \Theta(\tau))
\]

\[
P_-^{(-3)}(t) = -2i\mu^3(\sigma_- \cdot \vec{A}_2)(\sigma_- \cdot \vec{A}_1)^*(e^{i\omega_k t - \gamma t} \Theta(t - \tau) \Theta(\tau))
\]

In the \( xx \) configuration, \( \vec{A}_1 = \frac{1}{2} A_1 (\sigma_+ + \sigma_-), \vec{A}_2 = \frac{1}{2} A_2 (\sigma_+ + \sigma_-) \) and, therefore, the magnitude of the diffracting polarization density is

\[
|\vec{P}|^{(-3)} = \sum_k \frac{1}{2} \text{Re}[\mu^4 A_2^2 A_1^*](\sigma_+ + \sigma_-)
\]

The difference between \( xx \) and \( xy \) is the orientation of the exciton polarizations as a function of space in the sample, since the direction of the electric field is a function of position for \( xy \) but not for \( xx \). Clearly, the electric field is \( z \) polarized everywhere in the \( xx \) configuration. In the \( xy \) configuration, the electric field polarization state in the medium, for temporally overlapped pulses, is

\[
\vec{E} = \vec{e}_z e^{i\vec{K}_1 \cdot \vec{r}} + \vec{e}_y e^{i\vec{K}_2 \cdot \vec{r}}
\]

which can be expressed in terms of the phase angle

\[
\theta = \frac{1}{2}(\vec{K}_1 - \vec{K}_2) \cdot \vec{r}
\]

as

\[
\vec{E} = \frac{1}{2} e^{i(\vec{K}_1 + \vec{K}_2) \cdot \vec{r}/2} \left( \sigma_+ (e^{i\theta} - ie^{-i\theta}) + \sigma_- (e^{i\theta} + ie^{-i\theta}) \right).
\]

For the \( xy \) configuration, \( \vec{A}_1 = \frac{1}{2} A_1 (\sigma_+ + \sigma_-), \vec{A}_2 = \frac{1}{2} A_2 (\sigma_+ - \sigma_-) \) and, the magnitude of the diffracting polarization density is

\[
|\vec{P}|^{(-3)} = \sum_k -\frac{1}{8} \text{Re}[\mu^4 A_2^2 A_1^*](\sigma_+ + \sigma_-)
\]

Therefore, the diffracted power measured in a FWM experiment, which is proportional to \( |\vec{P}|^{(-3)}|^2 \), from a collection of three-level systems in the non-interacting limit is predicted to be the same for both polarization configurations and the polarization of the diffracted beam is also predicted to be the same.
2.4 FWM for interacting excitons and continuum states

In the low density limit, where interactions between electron-hole pairs can be neglected, the SBE reduce to an uncoupled set of OBE for excitons and continuum excitations. To investigate the effects of exciton-continuum interactions with the SBE, the low density limit cannot be used. However if the occupations cannot be assumed to be zero, the SBE must be solved numerically because of the coupling between all states. Numerical solutions in this regime have been presented and used to interpret experimental results in terms of exciton-continuum interactions\cite{17, 25}. However, numerical solution of the SBE is beyond the scope of this thesis. The approach taken here is to investigate the applicability of two simple models that extend the OBE to account phenomenologically for effects due to exciton-continuum scattering.

The first part of this section outlines how the effects of interactions between excitons and continuum excitations can be included in a model of coherent exciton dynamics. The dominant effect of exciton-continuum scattering is assumed to be an increased exciton dephasing rate. Justification for this assumption cannot be provided by identifying dominant terms in the SBE because the basis is not an exciton basis. The polarization of continuum excitations is very short lived\cite{11} and thus should perturb the exciton states only weakly compared to the effect of continuum populations, which are much longer lived. Thus effects due to incoherent exciton-carrier scattering are assumed to dominate effects due to coherent exciton-continuum coupling in this model, which is outlined in section 2.4.1.

In the second part of this section, exciton-continuum interactions are discussed for the case of energetically degenerate exciton and continuum states. The SBE are derived from a two-band model and therefore are inadequate to model the interactions between electrons in different bands. To investigate the interaction between the split-off exciton and continuum excitations of the heavy and light hole bands, a multiple band model is needed. Although models which include the heavy and light hole bands for coherent dynamics have been presented in the literature\cite{60, 65, 66}, none have included the split-off band. In section 2.4.2, a simple model of coherent dynamics is presented which accounts for the interaction of split-off excitons with continuum excitations of heavy and light hole bands.
2.4.1 Excitation-induced dephasing

The interaction of excitons with free carriers causes the exciton dephasing rate $\gamma_x$ to be density dependent and is important for conditions that excite both the continuum and exciton states. For temporally overlapped pulses that are polarized in the same direction, interference of the electric fields results in a spatial modulation of the total carrier density, which causes a spatial modulation of $\gamma_x$ and leads to an additional source of diffraction for excitons. This diffraction mechanism is called excitation-induced dephasing (EID) [19, 20, 67] and can be described by a simple extension of the OBE[20]. In this section, an expression is derived for the density dependence of the FWM exciton emission due to EID.

The dynamics of the exciton polarization as described by the OBE is

$$\left(\frac{\partial}{\partial t} + iv_x + \gamma_x\right)P_x = i(1 - 2f_x)\frac{\mu_x E(t)}{\hbar}. \tag{2.43}$$

To illustrate the main aspects of EID, the exciton dephasing rate is taken to have the following functional dependence on carrier density, $N$.

$$\gamma_x(N) = \gamma_x^0 + \Gamma_x N \tag{2.44}$$

where $\Gamma_x$ is proportional to the exciton-carrier scattering cross section and $\gamma_x^0$ accounts for all density-independent scattering processes. The total carrier density is $N = \sum_k f_k$ and has spatial Fourier components of the same wave vectors as $f_k$, i.e. $N^{(0)}$ and $N^{(\pm 2)}$. The rate equation for the diffraction component, $P_x^{(-3)}$, has an additional driving term as a result of the spatial modulation of $N$. Each driving term can be identified as a source of emission and is connected to a physical process. The sources of emission are categorized into two types: electric field scattering and polarization wave scattering. Free induction decay is an electric field scattering mechanism whereas EID is a polarization wave scattering mechanism. The following relation lists the driving terms for $P_x^{(-3)}$ and identifies the diffraction mechanism for each term:

$$\left(\frac{\partial}{\partial t} + iv_x + \gamma_x^0 + \Gamma_x N^{(0)}\right)P_x^{(-3)} = -2i f_x^{(-2)}\Omega^{(-1)} \quad \text{FID}$$

$$-P_x^{(-1)}\Gamma_x N^{(-2)} \quad \text{EID}. \tag{2.45}$$

The dominant source of diffraction depends on the excitation conditions. EID can be a very efficient mechanism for excitons when continuum transitions are simultaneously excited.
In order to focus on the EID mechanism, as opposed to FID, the excitation conditions are designed to produce a very low density of excitons and a high density of continuum excitations by tuning the laser to an energy well above the exciton energy. Therefore, the dynamics of the exciton polarization is assumed to be unaffected by the occupation $f_e$; the dynamics of $f_e$ is not calculated and $f_e$ is assumed to be zero. The temporal dynamics of the diffraction component $P_x^{(-3)}$ is determined by $P_x^{(-1)}$ and $\mathcal{V}^{(-2)}$, as can be seen from Eq. 2.45. Analytic expressions for $P_x^{(-3)}$, $P_x^{(-1)}$ and $\mathcal{V}^{(-2)}$ can be obtained by assuming the optical pulses are Dirac delta functions of time\cite{22} with the following notation (which is simplified from the previous definition in section 2.3.1 since the vector nature of the field is not important here):

$$\Omega^{(1)} = A_1 \delta(t + \tau)$$
$$\Omega^{(-1)} = A_2 \delta(t).$$

The continuum occupation modulation is

$$f_k^{(-2)} = A_1^* A_2 e^{-i\omega_k \tau - \gamma_k |\tau| \left[ \Theta(\tau) \Theta(t - \tau) + \Theta(-\tau) \Theta(t) \right]}$$

where $\Theta(t)$ is the Heaviside step function. The total carrier density modulation is, therefore,

$$\mathcal{V}^{(-2)} = \sum_k f_k^{(-2)} = A_1^* A_2 e^{-\gamma |\tau| \left[ \Theta(\tau) \Theta(t) \right]} \times \mathcal{V} \mu^2$$

With the assumption that the total diffracted power is very small compared to the total power in the transmitted beam, the component $P_x^{(-1)}$ is

$$P_x^{(-1)} = i A_2 e^{-i\omega \tau} e^{-(\gamma \tau + \Gamma_x N) t}.$$ 

The temporal profile of the diffraction component is, therefore,

$$P_x^{(-3)}(t) = -i A_2 \Gamma_x \mathcal{V} \mu^2 t e^{-i\omega \tau} e^{-(\gamma \tau + \Gamma_x N) t} \Theta(t) \delta(\tau)$$

which increases with time initially and then decays at longer times. This temporal profile is different from the profile produced by the FID mechanism, which was illustrated in Fig. 2.3. For EID a diffracting component $P_x^{(-3)}$ is "burned into" $P_x^{(-1)}$ as the exciton polarization density decays, whereas for FID the diffracting component is generated during the second pulse. The spectral profile of exciton emission is therefore different for the EID and FID
mechanisms. The exciton emission has a squared Lorentzian profile for the EID mechanism and a Lorentzian profile for the FID mechanism[22]. The spectral width of the emission is determined by the spatially averaged dephasing rate of the exciton, which can be much lower than the inverse of the pulse width. The diffraction efficiency of EID is determined by the total carrier density grating $N^{(-2)}$, which in the case of continuum excitation is non-zero only for temporally overlapped and similarly polarized pulses, as discussed in section 2.3. This is not the result of fast dephasing for the continuum states but is directly related to the bandwidth of excitation. Therefore, emission due to the EID mechanism is pulse-width limited versus delay if the excitation bandwidth is not limited by the absorption spectrum.

The different temporal profile also results in a different density dependence of the diffracted power. The diffracted energy per pulse is determined with the use of Eq. 2.31 and for the EID mechanism has the following dependence on excitation density:

$$J_{EID} \sim \frac{[\Gamma_x N]^2 \mu^2 V}{(\gamma_x^2 + \Gamma_x N)^3}. \quad (2.52)$$

At low density, $J_{EID}$ scales cubically with density but saturates as density increases and has a markedly different saturation behaviour than FID, which scales as $N^3 \mu^2 / (\gamma_x^2 + \Gamma_x N)$. The simple model for the exciton dephasing rate, which was given in Eq. 2.44, is likely to be applicable only over a certain density range, i.e. $\Gamma_x$ is a function of density. Eq. 2.52 is valid for a linear dependence of $\gamma_x(N)$ on density as given by Eq. 2.44. Due to screening the exciton-carrier scattering cross section decreases as density increases. If $\gamma_x(N)$ saturates at high density then the expression for $J_{EID}$ (Eq. 2.52) must be modified by replacing the factor in square brackets with the amplitude of the line width grating, $\gamma_x^{(-2)}(N)$, which is determined by the following expression:

$$\gamma_x^{(-2)}(N) = \frac{Q}{\pi} \int_0^{\pi/Q} \cos(2Qy)\gamma_x(N^{(0)} + 2N^{(-2)} \cos(2Qy))dy \quad (2.53)$$

where $y$ is the spatial dimension in the direction of the grating wave vector, $2Q$. Saturation of the line width grating implies that spatial frequencies higher than $2Q$ exist in the grating which cause diffraction into directions $\vec{k} - 5\vec{Q}$, $\vec{k} - 7\vec{Q}$ etc.

EID does not contribute a signal for cross-linearly polarized pulses, since the total density is spatially uniform in that case. The signatures of EID are: (i) spectrally narrow emission that is pulse width limited versus delay (and peaked at zero delay); (ii) a strong
dependence on polarization configuration: (iii) a different density dependence than free
induction decay.

2.4.2 Fano resonance at the SO band edge

Since the SO band edge is at lower energy than the HH and LH band edge, excitons
associated with the SO band are energetically degenerate with continuum excitations in-
volving the HH and LH bands. If an interaction exists between the split-off exciton and
optically coupled LH or HH continuum excitations, then neither the split-off exciton nor
continuum excitations are an appropriate basis of states to describe optical excitation. The
optically coupled states must be considered to be a combination of split-off exciton and
continuum states, which is referred to as a Fano resonance. A new basis of eigenstates can
be obtained by diagonalization of the Hamiltonian that includes the interaction between
split-off excitons and continuum excitations. The coherent response can be calculated by
modeling the temporal dynamics of the new basis states in the context of the OBE. The
new basis is only necessary if the interaction couples the split-off exciton to optically active
continuum states, which is assumed to be the case here. Otherwise the interaction could
be included phenomenologically in the polarization dephasing rate for the split-off exciton.
In this section, a model of FWM at a Fano resonance that was developed by Meier et al.
[68] specifically for the case of ultrashort pulse excitation is outlined.

The model discussed here for a Fano resonance at the split-off transition energy is based
on the following Hamiltonian.

\[ H = H_{so} + H_{hh} + V_{int} \]  (2.54)

where \( H_{so} (H_{hh}) \) is the Hamiltonian for a two-band model that describes the split-off (heavy
hole) and conduction bands. The light hole band is neglected to avoid the complication of
coupling to more than one continuum[26]. \( V_{int} \) represents an interaction between split-off
states and heavy hole states. The only states that are considered in the model are the
split-off exciton, \( |SO\rangle \), and the HH continuum states, which are labeled by the energy,
\( \varepsilon \), as \( |C(\varepsilon)\rangle \). The continuum states are characterized by a density of states, \( g \), and the
split-off exciton energy is \( \varepsilon_s \). The dipole moments for transitions from the ground state
to the split-off exciton and continuum states are denoted as \( \mu_s \) and \( \mu_c \). The interaction
Hamiltonian between exciton and continuum states, $V_{\text{int}}$, is taken to be of arbitrary origin and to have matrix elements

$$\langle C(\varepsilon)|V_{\text{int}}|SO \rangle = V_F$$

(2.55)

that are assumed to be independent of energy. The inverse lifetime of the split-off exciton due to decay to the continuum is $2\pi g V_F^2/\hbar$. Fano[28] showed that the eigenstates of $H$ are

$$|\psi(\varepsilon)\rangle = \frac{\sin \Delta}{\pi g V_F} |SO\rangle - \cos \Delta |C(\varepsilon)\rangle$$

(2.56)

and that the dipole moments for transitions from the ground state to these states are

$$\mu = \frac{\sin \Delta}{\pi g V_F} \mu_x - \cos \Delta \mu_c$$

(2.57)

where $\tan(-\Delta) = \pi g V_F^2/(\varepsilon - \varepsilon_x)$. The states $|\psi(\varepsilon)\rangle$ represent a continuum of energy levels. To simplify the notation the parameter $q$ is defined as the ratio of dipole moments for the discrete state and for an energy range of the continuum given by the interaction energy

$$q = \frac{1}{\pi g V_F} \frac{\mu_x}{\mu_c}$$

(2.58)

and the reduced energy variable, $\bar{\varepsilon}$, is defined as

$$\bar{\varepsilon} = -\frac{\cos \Delta}{\sin \Delta} = \frac{\varepsilon - \varepsilon_x}{\pi g V_F^2}.$$  

(2.59)

The linear absorption spectrum is proportional to $|\mu(\varepsilon)|^2$ which is

$$|\mu(\varepsilon)|^2 = \frac{(q + \bar{\varepsilon})^2}{1 + \bar{\varepsilon}^2} |\mu_c|^2$$

(2.60)

and is profoundly affected by interference between transition amplitudes of the discrete and continuum states. The characteristic spectral profile of Eq. 2.60 is asymmetric and called a Fano profile. An example of the linear absorption spectrum normalized by $|\mu_c|^2$ is shown in Fig. 2.5.

The coherent dynamics of a Fano resonance, as represented by the model described above, have been calculated by Meier et al. in the context of the OBE[68], i.e. the Coulomb interaction between electrons is neglected. The set of states, $|\psi(\varepsilon)\rangle$ plus the ground state, are treated as an M-level system as opposed to a set of M two-level systems. Thus the equations of motion for the density matrix of the M-level system are extended from the
OBE introduced earlier in this chapter to include rate equations for the coherence between continuum states. The equations of motion for this model are

\[
\left( \frac{\partial}{\partial t} + i\nu_\epsilon \right) P_\epsilon = iE(t)\mu(\varepsilon)f_\gamma - iE(t)\sum_{\epsilon'}\mu(\varepsilon)f_{\epsilon,\epsilon'} \tag{2.61}
\]

\[
\left( \frac{\partial}{\partial t} + i(\nu_\epsilon - \nu_{\epsilon'}) \right) f_{\epsilon,\epsilon'} = iE(t)\mu(\varepsilon)P_{\epsilon,\epsilon'}^* - iE(t)\mu^*(\varepsilon')P_\epsilon \tag{2.62}
\]

\[
\frac{\partial}{\partial t} f_\gamma = iE(t)\sum_\varepsilon \mu^*(\varepsilon)P_\epsilon - iE(t)\sum_\varepsilon \mu(\varepsilon)P_\epsilon^* \tag{2.63}
\]

where \(f_{\epsilon,\epsilon'}\) is the coherence between continuum states and \(f_{\epsilon,\epsilon}(f_\gamma)\) is the occupation of state \(|\psi(\varepsilon)\rangle\) (ground state). In this model, the dephasing rate is assumed to be zero. For delta function pulses, Meier et al. showed that the result for the FWM spectrum at zero delay is

\[
S(\varepsilon, \tau = 0) \propto \frac{q^4 + (2q + \varepsilon)^2}{1 + \varepsilon^2} |\mu_c|^4. \tag{2.64}
\]

Experimental results will be compared to the predictions of Eq. 2.64. Fig. 2.5 shows an example of the FWM spectrum calculated with Eq. 2.64 normalized by \(|\mu_c|^4\).

Meier et al. also found the temporal dynamics of the polarization to be affected by interference, which is most noticeable for small values of \(q\). The total diffracted power, \(J(\tau)\), is predicted to have a minimum at a finite positive value of \(\tau\). i.e. \(J(\tau)\) exhibits non-exponential decay. Meier et al. pointed out that this prediction for \(J(\tau)\) cannot be obtained analytically by assuming delta function pulses. Their numerical results for realistic pulse durations clearly demonstrate the predicted behaviour. Since there is no analytic formula for characteristic features of the SI-FWM trace, experimental results cannot be compared quantitatively to this prediction. However for larger values of \(q\), Meier et al. predicted that the minimum would become just a dip in the trace and would vanish at large \(q\).

FWM experiments were performed for parallel and perpendicularly polarized pulses as a part of this thesis. The polarization dependence of FWM at a Fano resonance was not addressed by Meier et al., since they did not specify a basis based on the polarization of the electric field. Therefore, a simple model was developed to analyze whether or not a Fano profile should be observed in the FWM spectrum for both polarization orientations. It was shown in section 2.3.1 that a three-level system is required to model the dependence on electric field polarization directions and that a convenient set of basis states are right and left circularly polarized states. The basis states of \(H_{so} + H_{hh}\) are depicted in Fig. 2.6.
Figure 2.5: Linear absorption spectrum (dashed curve) and FWM spectrum (solid curve) for a Fano resonance with $q = 1$. 
Figure 2.6: Energy level diagram of the split-off exciton and continuum states in the circularly polarized basis. The labels beside the vertical arrows indicate the polarization that induces a specific transition.

for just the split-off exciton states and HH continuum states, which are labeled with a + (-) symbol for right (left) polarization. The allowed optical transitions for both right and left circularly polarized light are indicated by the symbols beside the vertical arrows. The split-off exciton and continuum state wavefunctions are, therefore,

\[ |C\rangle = c_+ |C, +\rangle + c_- |C, -\rangle \]

\[ |X_{so}\rangle = s_+ |SO, +\rangle + s_- |SO, -\rangle. \]

The interaction Hamiltonian between exciton and continuum states, \( V_{int} \), is again taken to be of arbitrary origin and to have the following matrix elements:

\[ \langle C, +|V_{int}|SO, +\rangle = \langle C, -|V_{int}|SO, -\rangle = V_A \]

\[ \langle C, +|V_{int}|SO, -\rangle = \langle C, -|V_{int}|SO, +\rangle = V_B. \]

In order to simplify the model, each split-off exciton state is assumed to interact with only one continuum. If \( V_A \) is assumed to be zero, the eigenstates of \( H_{so} + H_{hh} + V_{int} \) are

\[ |\psi_1(\varepsilon)\rangle = \frac{\sin \Delta}{\pi g V_B} |SO, +\rangle - \cos \Delta |C, -\rangle \]

\[ |\psi_2(\varepsilon)\rangle = \frac{\sin \Delta}{\pi g V_B} |SO, -\rangle - \cos \Delta |C, +\rangle \]
Chapter 2. Theory

and the dipole moments for transitions to these states are

\[ \bar{\mu}_1 = \frac{\sin \Delta}{\pi g V_B} \mu \sigma_+ - \cos \Delta \mu \sigma_- \]

\[ \bar{\mu}_2 = \frac{\sin \Delta}{\pi g V_B} \mu \sigma_+ - \cos \Delta \mu \sigma_- \]

The total polarization density emitting in the diffracted direction is, therefore,

\[ \tilde{P}^{(-3)} = \text{trace}(\rho \tilde{\mu}) = \sum_\varepsilon [\bar{\mu}_1 P_1^{(-3)} + \bar{\mu}_2 P_2^{(-3)} + \bar{\mu}_1^* P_1^{*(-3)} + \bar{\mu}_2^* P_2^{*(-3)}] \]

The diffraction components of the polarization density can be obtained by solving the system of equations 2.26-2.30, (which is a simplified set of equations compared to the model used by Meier et al.) for \( P_1^{(-3)}(\varepsilon) \) and \( P_2^{(-3)}(\varepsilon) \) separately. Analytic expressions are obtained if the optical pulses are assumed to be Dirac delta functions of time, i.e. \( E^{(1)}(t) = A_1 \delta(t + \tau) \) and \( E^{(-1)}(t) = A_2 \delta(t) \). In the limit of a zero dephasing rate, the diffraction components are:

\[ P_1^{(-3)}(\varepsilon, t) = -2i(\mu_1(\varepsilon) \cdot A_2)e^{-i(\varepsilon - r)/\hbar}(\mu_1(\varepsilon) \cdot A_2)(\mu_1(\varepsilon) \cdot A_1)^* \Theta(t)\Theta(\tau) \]

\[ P_2^{(-3)}(\varepsilon, t) = -2i(\mu_2(\varepsilon) \cdot A_2)e^{-i(\varepsilon - r)/\hbar}(\mu_2(\varepsilon) \cdot A_2)(\mu_2(\varepsilon) \cdot A_1)^* \Theta(t)\Theta(\tau) \]

where \( \Theta(t) \) is the Heaviside function. In the limit of long dephasing times, the power spectrum of the diffracted pulse can easily be obtained because each component is essentially a plane wave. Therefore, the FWM spectrum at energy \( \varepsilon \) is determined only by the magnitude of the polarization components at \( \varepsilon \). In the \( xx \) configuration, \( \bar{\lambda}_1 = -\frac{1}{2}A_1(\sigma_+ + \sigma_-) \), \( \bar{\lambda}_2 = -\frac{1}{2}A_2(\sigma_+ + \sigma_-) \) and, therefore, the magnitude of the diffracting polarization density is

\[ \tilde{P}^{(-3)}(t) = \sum_\varepsilon \frac{1}{8} \text{Re}[(\mu_1^2 A_2^2 A_1^*)] \frac{(q + \bar{\varepsilon})^4}{(1 + \bar{\varepsilon}^2)^2} (\sigma_+ + \sigma_-) e^{-i(\varepsilon - r)/\hbar} \Theta(t)\Theta(\tau) \]

which shows that the FWM spectrum is predicted to be the fourth power of the linear spectrum (Eq. 2.60) in this simple model. For the \( xy \) configuration, \( \bar{\lambda}_1 = -\frac{1}{2}A_1(\sigma_+ + \sigma_-) \), \( \bar{\lambda}_2 = -\frac{1}{2}A_2(\sigma_+ - \sigma_-) \) and, the magnitude of the diffracting polarization density is

\[ \tilde{P}^{(-3)}(t) = \sum_\varepsilon \frac{1}{8} \text{Re}[(\mu_1^2 A_2^2 A_1^*)] \frac{(q^2 - \bar{\varepsilon}^2)^2}{(1 + \bar{\varepsilon}^2)^2} (\sigma_+ + \sigma_-) e^{-i(\varepsilon - r)/\hbar} \Theta(t)\Theta(\tau) \]

which is clearly different from the \( xx \) case. However, interference minima are predicted by this model for the \( xy \) case at \( \bar{\varepsilon} = \pm q \).
In the model described above, the interaction matrix elements between similarly polarized split-off exciton and continuum states, $V_A$, was assumed to be zero to simplify the analysis. If $V_B$ had been set to zero instead of $V_A$, the wavefunctions $|\psi_1\rangle$ and $|\psi_2\rangle$ would have been pure $\sigma_+$ and $\sigma_-$ states, instead of the mixtures given by Eqs. 2.69 and 2.70. An analysis of the dependence on electric field polarization configuration for the case $V_B = 0$ follows the same procedure outlined above. The result for delta function pulses is that both $xx$ and $xy$ configurations produce a $\tilde{P}(-3)$ given by Eq. 2.76 and, therefore, the same FWM spectrum. The purpose of this section was to demonstrate that, within the context of the simple model outlined here, the two polarization configurations do not necessarily produce the same FWM spectrum. One possible requirement for observation of different FWM spectra is that the matrix elements of the interaction between split-off excitons and continuum states not all be equal.

In summary, three models have been presented to describe the coherent response of a semiconductor to optical radiation. The continuum states can be modeled with the OBE but since the dephasing rate is typically very high, numerical solutions are required to account for convolution with the pulse profile. The EID model is appropriate for the exciton response when a large bandwidth of continuum excitations is simultaneously excited. A model of the exciton response for isolated excitation was not presented because this case has been investigated previously. The coherent response near a Fano resonance can be modeled within the context of the OBE if the dipole moments of the distribution of states are modified to account for the interaction with the continuum.
Chapter 3

Experimental Apparatus

In this chapter the techniques and apparatus used to measure the polarization dephasing rate of electronic excitations are described in detail. The general experimental technique was two-pulse, self-diffracted four-wave mixing (FWM), in which two pulses excite the sample and the beam diffracted into the phase-matched direction is detected as a function of the temporal delay between excitation pulses. Two types of FWM experiments were performed: spectrally integrated (SI-FWM) and spectrally resolved (SR-FWM). The temporal resolution required to resolve the dephasing dynamics of continuum excitations in semiconductors is of the order 10 fs\[11\]. At the initiation of this project commercial laser systems were not available with pulse widths below 100 fs. However, several laboratories around the world had reported the production of pulses in the near infra-red with pulse widths in the range 30–60 fs\[69, 70, 71, 72, 73\]. Based on the general guidelines of these reports, I designed and constructed a 30-fs, mode-locked, Titanium-doped-sapphire laser.

An outline of the laser design considerations is provided here along with a description of the laser. A thorough characterization of the operating specifications was done but only some representative results are presented here. A procedure to align the laser for mode-locked operation is presented in appendix A. The apparatus used to perform FWM experiments is discussed in detail. All the electronic circuits used for the detectors are described in appendix B. The procedures used to obtain and assess an optically thin InP sample are discussed in the final section along with sample characterization results.

3.1 Laser system

The source of tunable ultrashort optical pulses was a passively-mode-locked Ti:sapphire laser (Ti:S) that was pumped by a continuous wave (CW) argon ion laser. The Ti:S laser
produced 30 fs pulses tunable in the range 0.84 μm to 0.80 μm (1.47 eV to 1.55 eV) at 84 MHz with 300 mW average power. A wider tuning range and higher output power were achievable with longer pulses. The laser design is based on the Kerr-lens mode-locking mechanism, which was discovered in 1990[74]. Several published papers discuss the physical mechanism of Kerr-lens mode locking (KLM) and general design criteria for Ti:S lasers[69, 75, 76, 77, 78, 79]. Only an overview of the design considerations and a brief explanation of KLM are presented here.

The standard method used to generate ultrashort optical pulses is mode-locking, which is the process of establishing and maintaining a phase relationship for a large number of modes. In the case of a laser the modes have the frequencies of the standing-wave cavity modes. The phase relationship is achieved by modulating the power in each mode at the cavity frequency; this ensures the sidebands overlap adjacent modes. This laser was designed to operate on gain modulation. The physical basis of KLM is the intensity-dependent index of refraction of the laser host material, sapphire, which causes self-focusing inside the gain medium for intense beams. The spatial mode of the cavity is different for CW and mode-locked (ML) operation because of the presence of the “Kerr lens” for the ML mode. The key design criterion is to have higher gain for the ML mode. Since the Ti:S crystal is pumped by a laser, the gain volume has a nominal Gaussian profile in the plane perpendicular to the cavity axis. Provided the gain is not heavily saturated, higher gain is achieved for a more tightly focussed mode in the gain volume. The cavity was designed to have a reduced mode size in the gain volume as a result of the self-focusing effect. Since the gain modulation is provided by the pulse itself, this is called passive mode locking and no cavity frequency stabilization is required.

A general design guideline for mode-locked Ti:S lasers is to have a phase shift across the gain region due to the intensity-dependent index of refraction of approximately 3. in order to provide sufficient discrimination between CW and ML gain[80]. The phase shift is $2\pi L n_2 I / \lambda$, where the gain length is $L$, intensity is $I$, wavelength is $\lambda$ and the intensity-dependent index of refraction parameter is $n_2 = 3 \times 10^{-16}$ cm$^2$/W for sapphire[81]. For typical cavity parameters, the pulse width must be of the order 100 fs and the spot size must be of the order of 25 μm diameter to satisfy this condition. The group delay dispersion of a few mm of sapphire is too large to support 100 fs pulses. A negatively-dispersive optical
element(s) is required inside the cavity to compensate for the material dispersion. A prism pair is used for this purpose[82, 83].

The pump laser is a Coherent Innova 310 argon-ion laser operating on all lines (the \( \lambda = 488 \) and 514 nm lines contain the majority of the power) and typically provides 4.5 W power. The polarization of the pump beam is rotated by 90° to be horizontal by a right-angled periscope, in order to minimize the reflection loss at the crystal face: the beam is focussed into the crystal by a 12 cm focal length lens.

The laser cavity is an asymmetric, 4-mirror, X-folded cavity with the gain medium in the tightly focussed section and the prism pair in the longer arm. In Fig. 3.1 is a schematic layout of the laser cavity, pump coupling optics, and some external optics. The laser crystal was purchased from Crystal Systems and is a Brewster-angled rectangular cylinder with dimensions: 8 mm path length, 1.5 mm height, and 2.6 mm width (3 mm width measured along the Brewster face). The Ti-doping density was specified to provide 85% pump absorption (i.e. an absorption coefficient at 0.5 \( \mu m \) of 2.5 cm\(^{-1} \)). The laser rod is clamped securely in a copper housing that contacts 4 faces and allows optical access to both polished end faces. The rod housing is mounted on a water-cooled heat sink. The specifications for the optics are listed in Table 3.1. The thickness of the output coupler was 0.125 inch to minimize the material dispersion for the pulses coupled out of the cavity. The prisms P1 and P2 are made of LaKL21 glass with an apex angle of 63.00°. The distance between the tips of the prisms is 43 cm and the amount of prism insertion is typically 1 mm and 2 mm for P1 and P2. The amount of prism insertion is controllable by translation along the direction that bisects the apex angle. A slit is placed in the dispersed region of the cavity; the wavelength is tuned by translating the slit horizontally. Two beams (beam 2 and 3) are split-off from the output beam and used to monitor the ML operation and for characterization purposes. The main beam (beam 1) is directed to the experimental apparatus.

Many of the optics are mounted on translation stages to allow adjustments of the cavity dimensions. In particular, the laser crystal and mirror M2 are translatable along the cavity axis. The dimensions which are critical for defining a stable cavity are the distances from the curved mirrors to the faces of the rod. These distances are labeled a and b in Fig. 3.1. For a given length of the rod and radius of curvature of the mirrors, there are regions in
Figure 3.1: Schematic top view of Ti:S laser. The lower part shows an enlarged view of the circled section. The cavity mirrors are: a high reflector (HR), an output coupler (OC) and two curved turning mirrors (M1 and M2). The specifications for the cavity mirrors are listed in Table 3.1. Two intracavity prisms (P1 and P2) provide negative group velocity dispersion. The output beam passes through a beam splitter, an external dispersion compensator (prisms P3 and P4) and a polarization rotator. a and b are dimensions referred to in the text. Ps: periscope. RPs: polarization rotating periscope. L: lens.
Table 3.1: Specifications for laser mirrors as labeled in Fig. 3.1. ROC: radius of curvature. Coating definitions are HR: high reflectivity, HT: high transmission, AR: anti-reflection. R: reflectivity. Numbers refer to wavelength in nm. *This mirror was obtained from Coherent Laser Systems Inc., Palo Alto, CA.

the $ab$ parameter space where the cavity is stable. In general, there will be two stability zones, since the cavity is asymmetric. The effect of the Kerr lens is to change the location of these stability zones. The key to aligning the laser for ML is to find the optimal location in the $ab$ parameter space that provides good discrimination against the CW mode and good ML output power and mode quality. The location for best ML operation was found to be at smaller values of the $b$ dimension relative to the optimal CW location.

### 3.1.1 Characterization

The characteristic of primary importance is the pulse width, which was measured by intensity autocorrelation using a background-free second-harmonic (SH) generation technique[84, 85], with a 100 $\mu$m thick KDP crystal. The apparatus used for the FWM experiments was also used for the autocorrelation measurement (see section 3.2). The SH light was detected with a Si avalanche photodiode. A typical autocorrelation is shown in Fig. 3.2(a). The pulse width is estimated by assuming a temporal profile for the pulse intensity. For a profile

$$I(t) = I_0 \text{sech}^2(1.76 t/\tau_p), \quad (3.1)$$

the pulse width $\tau_p$ is 65% of the full width at half maximum (FWHM) of the intensity autocorrelation. For this example, the pulse width is 30 fs.
The spectral content of beam 2 was monitored with a detector array at the output of a monochromator. A rough assessment of chirp is provided by the product of pulse width and bandwidth, if the temporal profile is known. Typically the time-bandwidth product was measured to be 1.7 eV-fs. For the temporal shape given in Eq. 3.1, the transform-limited time-bandwidth product is 1.3 eV-fs ($\Delta \nu \tau_p = 0.32$)[86]. The difference could be attributed to chirp or to a different profile than assumed. A better assessment of chirp results from an interferometric autocorrelation[86]. The same doubling crystal as used for the intensity autocorrelations was placed at the output port of a Michelson interferometer. The SH light was detected with a photomultiplier tube (1P28). Fig. 3.2(b) shows the interferometric autocorrelation. The fringe resolution extends over the full width, which indicates that the pulse is very close to transform limited.

The stability of the laser for maintaining ML operation was limited by random fluctuations of pump laser power, vibrations of the optical mounts due to table vibrations or air currents, and beam interruption by dust. The duration of uninterrupted ML operation was typically 1 hour.

### 3.1.2 Dispersion compensation

The bandwidth of a 30 fs pulse is so large that the difference in group velocity over the bandwidth in glass is not negligible. Dispersion compensation was necessary for these experiments because the pulses propagated through about 3 cm of glass before the sample. The external dispersion compensator is a sequence of two SF10 prisms (apex angle is $60.65^\circ$) and is shown in Fig. 3.1 as prisms P3 and P4. The compensator is located near the laser for the convenience of using P-polarized light. The distance between the tips is 29 cm. The amount of prism insertion was adjusted to optimize the autocorrelation width.
Figure 3.2: (a) Intensity autocorrelation and (b) interferometric autocorrelation. In (a) the zero of delay axis is defined as the peak of the trace. In (b) the zero of delay is not specified.
Table 3.2: Characterization of the $\lambda/2$-plate used to rotate the polarization of the probe beam. The ratio of the power polarized in orthogonal directions is a measure of the ellipticity of the probe polarization. At 801 nm the $\lambda/2$-plate introduces a small degree of ellipticity.

3.2 Experimental arrangements

Both SR-FWM and SI-FWM experiments used the same apparatus with different detection systems. The FWM apparatus consists of a spatial filter, a variable-delay pump-probe set-up and a cryostat. The apparatus was specifically designed to implement a noise reduction scheme called rapid-scan, which is similar to lock-in detection but offers the advantages of less sensitivity to long term drift and an easier beam alignment procedure[87, 88].

The polarization of the Ti:S beam was rotated to vertical by a 90° periscope and directed to the experimental set-up shown in Fig. 3.3. A spatial filter was used to ensure a good beam spatial profile. The beam was focused through a 50 $\mu$m diameter pinhole with a 10 cm lens and collimated with a 7.5 cm lens. The beam was split into pump and probe beams of approximately equal amplitude (the amplitude ratio was wavelength dependent). A compensator plate was inserted into the pump to equalize the amount of glass in each beam. For some experiments the polarization of the probe was controlled with a $\lambda/2$-plate. The polarization state of the probe beam was characterized at five wavelengths for an orientation of the fast and slow axes of the $\lambda/2$-plate at 45° to the polarization direction of the incident field. The power ratios of the unrotated component to the rotated component of the probe beam for each wavelength are listed in Table 3.2. If polarization
control was not necessary, the $\lambda/2$-plate was removed. Translation of a retro-reflector provided a variable delay between pump and probe pulses. Both beams were focussed onto the sample at $\pm 1^\circ$ angle of incidence by the same lens ($f=50$ cm). Inside the sample, the beams propagate at approximately $0.3^\circ$ to the normal. Autocorrelations were measured by redirecting the two beams toward a frequency-doubling crystal (see section 3.1 for details). The doubling crystal was positioned at the point equidistant with the sample from the lens, which facilitated spatially overlapping the spots on the sample. The sample was placed in a cryostat equipped with two windows for optical access. The pressure in the cryostat was pumped down to approximately $5 \times 10^{-5}$ Torr by a cold-trapped diffusion pump. The vibrations of the pump were isolated from the cryostat by clamping the connection hose to a stable support. The cryostat was a flow-through type and liquid helium was continuously delivered via a transfer tube connected to a dewar. The sample was mounted in a copper housing and attached to the cold finger of the cryostat. The sample temperature was approximately 5 K for all FWM measurements.

The path length for the probe was varied at a frequency of 26 Hz by mounting a 0.5 inch diameter light-weight retro-reflector on the cone of a woofer speaker. The reduction in beam diameter provided by the lenses in the spatial filter facilitated alignment of the small retro-reflector. The direction of beam propagation was made parallel to the direction of speaker motion to avoid a systematic error related to correlated beam translation. The delay was rapidly scanned by driving the speaker at 26 Hz with a triangle wave from a power-amplified function generator. The frequency was selected to avoid vibration resonances of the breadboard, on which the apparatus was mounted. The output voltage of a detector was recorded using a National Instruments AT-MIO-16-F5 analog-to-digital converter (A/D) interfaced to a micro computer. The A/D was triggered by a pulse synchronized to the function generator with a variable phase delay. Successive scans were summed in computer memory to reduce noise; typically 5000 scans were averaged. The software used to control data acquisition was written by me. The system resolution is ultimately limited by the sample rate and speaker velocity. Better temporal resolution could be achieved by increasing the sample rate or decreasing the speaker velocity. The maximum sample rate of the A/D (200 ksamples/second) was used. The speaker velocity was typically 60 $\mu$m/msec, which gives a resolution of 1 fs. However, the frequency response of
Figure 3.3: Schematic layout of FWM experimental apparatus. Label definitions are:
f: lens focal length. BS: beam splitter. c: compensator. λ/2: half-wave retardation plate.
the detector electronics was intentionally limited to reduce noise. The actual bandwidth selected was dependent on detector type. Typically a resolution of 6 fs was obtained. The range of delay for a scan was typically 1 ps and 1000 conversions were made per scan. The motion of the speaker was determined to be linear over the full range of motion sampled by measuring the width of the autocorrelation trace as the zero delay position was scanned over the full range of speaker motion.

The diffracted beams were directed to a detection apparatus. For spectrally integrated measurements a Si pin diode was used. The sensitive area was 1 mm², which is small enough to serve as a spatial filter and reject some scattered light. At low excitation powers, the majority of the detected light was scattered from the surface of the sample. An identical diode was used to detect a reference beam (detector D2) and allowed subtraction of the background. Correlated noise due to laser instability was removed by optically balancing and electronically subtracting the currents from detectors D1 and D2. A 100 times amplifier and the internal 100 times amplifier of the A/D board gave a minimum detectable level of 15 fW. However, the signal-to-noise ratio was less than one at a power level of approximately 1 pW with 10,000 scans averaged. Thus the noise equivalent power was approximately 1 pW. (Note: 1 pW corresponds to 1 photon/pulse.)

For spectrally resolved measurements, the diffracted beam was focussed through a pinhole to reject scattered light and then focussed onto the entrance slit of a monochromator. The monochromator was equipped with a 590 lines/mm grating and had a focal length of 0.5 m. The spectral resolution was typically 1.3 meV. The output light was detected with a photomultiplier tube that was AC-coupled to reject background light. A subtraction system could not be used because most of the noise originated in the detector and could not be correlated to another detector. A full set of spectrally-resolved data required multiple traces of the diffracted power versus delay acquired over a range of wavelengths. The number of scans averaged at each wavelength was only 1000, in order that the full set of scans could be accumulated before the laser stopped mode-locked operation. The signal-to-noise ratio was significantly worse for SR-FWM compared to SI-FWM. The computer was also used to control the spectral position of the monochromator.

The excitation density \( N \) was estimated from the fluence \( F_0 \), absorption coefficient \( \alpha \).
photon energy $\hbar \omega_0$ and reflectivity $R$ using the following relation.

$$N = (1 - R) \frac{\alpha F_0}{\hbar \omega_0}.$$  \hspace{1cm} (3.2)

The surface density and average volume density are nearly equal since the sample is optically thin. Density values reported throughout this thesis are surface densities. The focussed spot size was determined by translating a knife edge across the beam and measuring the power transmitted. The radius was typically 100 $\mu$m. Experiments were performed over the range $N = 1 \times 10^{15}$ cm$^{-3}$ to $1.5 \times 10^{17}$ cm$^{-3}$.

### 3.3 Sample

The sample used for these experiments was a 0.3 $\mu$m single-crystal, thin film of Indium Phosphide. A thin sample was required because the experiments were performed in a transmission geometry. I acquired a heterostructure consisting of a 0.3 $\mu$m layer of InP and a 0.5 $\mu$m stop-etch layer of In$_x$Ga$_{1-x}$As grown on an InP(100) substrate from the Molecular Beam Epitaxy facility of the Ontario Centre for Materials Research. The thin InP film was isolated from the heterostructure by performing a two-step chemical etch procedure that first removed the InP substrate and then removed the stop-etch layer. For mechanical support the thin film was bonded to a sapphire window[89]. I performed all etching and mounting procedures. The chemical-etch procedure is described here in detail[90, 91]. The sample characterization results are presented and discussed briefly.

### 3.3.1 Etch procedure

The first step is to protect the thin InP layer from exposure to acid. The heterostructure was covered with a drop of a solution of Apiezon W (Black Wax) dissolved in trichloroethylene (TCE). The meniscus of the drop was gently broken so that the solution spilled over the edges and protected the sides of the thin layer as well. The Black Wax solution was allowed to air dry for 45 minutes and then placed in an oven at 170$^\circ$ C for 15 minutes.

The first acid is a solution of HCl:H$_3$PO$_4$ (3:1) that etches InP. The heterostructure was placed into a beaker with approximately 15 ml of solution for 1 hour. The etching is finished when bubbles cease to form on the surface. The thin two-layer structure was transferred to
a rinse beaker of deionized water. The second acid is a solution of HF:H₂O₂:H₂O (1:1:10). which etches InₓGa₁₋ₓAs but not InP. The stop-etch layer is removed very quickly. The sample was removed from the acid and rinsed in deionized water.

The thin film was placed on top of a drop of water on a sapphire window. The water drop was partially soaked up with bibulous paper, but some water was intentionally left under the InP film. The assembly was placed under an incandescent lamp overnight to dry. The Black Wax was dissolved in TCE and the thin film remained adhered to the sapphire window by van der Waals bonding[89].

3.3.2 Sample characterization

The quality of the sample was assessed by photoluminescence (PL) characterization, which is a measurement of the spectrum of light emitted from the sample when excited by laser illumination. The primary purpose of this characterization was to identify the excitonic resonance(s) and to estimate the exciton coherence time. An extensive analysis of the line shape and density dependence were not performed. A diagram of the apparatus used to measure the PL spectrum is shown in Fig. 3.4. The Ti:S laser was used at a photon energy of 1.51 eV in CW mode to excite the sample. The sample was mounted in the same cryostat used for FWM measurements and the temperature was held at 5 K. Scattered laser light was rejected with an iris and a polarizer. The same monochromator used for SR-FWM measurements was used with resolution of 0.5 meV. A photomultiplier (Hamamatsu R928) was used to detect the light. Fig. 3.5 shows the PL spectra for a range of excitation densities from 1 × 10¹³ cm⁻³ to 2 × 10¹⁵ cm⁻³, which were estimated by assuming a carrier lifetime of 1 ns. The features of the PL spectrum that are indicators of a good quality material are: (i) a sharp decrease of the density of states on the low energy side of the exciton resonance; (ii) a narrow spectral width; (iii) good luminescence efficiency; and (iv) stable peak position with increased excitation density.

The exciton peak is at 1.415 eV and does not shift as the excitation density is increased. The low energy side has an exponential dependence on energy (which is expected for an Urbach density of states) with an energy decay constant of 2 meV. The high energy side is Lorentzian and indicates the linewidth is 1 meV HWHM at the lowest density. This
corresponds to a dephasing time of 660 fs. The PL spectrum does not change shape below $2 \times 10^{14}$ cm$^{-3}$, although the resolution of the spectrometer was only 0.5 meV and did not allow a narrower linewidth to be determined. The dependence of the PL power on excitation density is nonlinear, which indicates that the non-radiative recombination rate is larger than the radiative rate at these densities. The main features of the PL spectrum are indicative of a good quality material.

A transmission spectrum was measured at 5 K with an unpolarized white light source over the range 1.3 to 1.6 eV, using the experimental arrangement shown in Fig. 3.6. The transmission spectrum is shown in Fig. 3.7. The resolution of the spectrum is low but the general features of the sample absorption are evident. The exciton is at 1.42 eV and appears very broad due to the low resolution. The split-off band edge is in the range 1.52–1.53 eV, which is close to the expected energy from the values listed in Table 2.1. Fabry-Perot effects are not evident because the sample is very thin and the beam had a large spread of wave vectors. Due to some cracks in the sample and the large size of the white light spot, the absolute transmission scale cannot be calibrated. The FWM experiments are unaffected by these defects because the focussed spot size of the laser beam is smaller than the distance between cracks. A suitable location on the sample was found where the scattered light was tolerable for FWM experiments.
Figure 3.4: Experimental arrangement to measure the photoluminescence spectrum. Label definitions are pol: polarizer, PMT: photomultiplier tube, Mono.: Monochromator.

Figure 3.5: Photoluminescence spectra at excitation densities from $1 \times 10^{13} \text{cm}^{-3}$ to $2 \times 10^{15} \text{cm}^{-3}$. Excitation photon energy was 1.51 eV.
Figure 3.6: Experimental apparatus used to measure the transmission spectrum. Mono.: Monochromator, OMA: optical multichannel analyzer.

Figure 3.7: Transmission spectrum measured at 5 K. The split-off band edge is labeled $E_0 + \Delta_0$. 
Chapter 4

Results and Discussion

In this chapter, results of FWM experiments performed over a range of excitation energy above the band gap of InP at 5 K are presented. The excitonic EID diffraction mechanism and the dephasing of continuum excitations near the band edge were investigated by exciting at 40 meV above the band gap. The coherent response at the \( E_0 + \Delta_0 \) band gap was investigated by tuning into resonance with the split-off band edge. In the first section, an overview of the main results is given. In subsequent sections, specific details of the results are interpreted in terms of physical scattering mechanisms. In section 4.2, the EID mechanism is investigated for the \( E_0 \) exciton under conditions of simultaneous free carrier excitation. In section 4.3, the continuum dephasing rate is measured near the band edge and is shown to increase abruptly at the threshold energy for LO phonon emission by electrons. In section 4.4, the coherent response near \( E_0 + \Delta_0 \) is investigated; a Fano-like spectral profile is observed in the spectrally resolved coherent emission at the \( E_0 + \Delta_0 \) band gap due to an interaction between \( E_0 + \Delta_0 \) excitons and continuum excitations of the heavy and light hole bands.

4.1 General Features

An overview of the coherent response above the band gap of InP is provided by the results of three SR-FWM experiments for excitation energies \( \hbar \omega_0 = 1.46, 1.49, 1.51 \) eV at a carrier density \( N \approx 1 \times 10^{17} \text{ cm}^{-3} \). The three tuning conditions of the laser spectrum are illustrated in Fig. 4.1 along with the sample transmission spectrum. In this section, the excitation pulses are polarized parallel to each other. SR-FWM results are presented for each excitation energy as both 3d and contour plots in the energy-delay (\( \hbar \omega_2, \tau \)) plane. The excitation energy is defined as the peak of the laser spectrum and is denoted \( \hbar \omega_0 \). The
Figure 4.1: The sample transmission spectrum (solid curve) at 5 K. Also shown are the excitation spectra for three photon energies, $\hbar \omega_0 = 1.46 \text{ eV}$ (circles), $\hbar \omega_0 = 1.49 \text{ eV}$ (squares), $\hbar \omega_0 = 1.51 \text{ eV}$ (triangles).

energy axes of the FWM spectra are referred to as $\hbar \omega$, to avoid confusion.

Fig. 4.2 shows the diffracted power spectrum for $\hbar \omega_0 = 1.46 \text{ eV}$ and $N = 5 \times 10^{16} \text{ cm}^{-3}$ obtained with 50 fs pulses. The diffracted signal is comprised of contributions from both the continuum states at $\hbar \omega_s \approx \hbar \omega_0$ and the exciton states at $\hbar \omega_s = 1.415 \text{ eV}$. The exciton diffraction is surprisingly large, given the small overlap of the laser spectrum with the exciton absorption line. The line width of the exciton emission is approximately 3 meV (full width at half maximum), which is close to the width measured by photoluminescence at similar average power. The area inside the contour at half-maximum of the exciton peak is 0.2 eV-fs and is much less than the area expected from the uncertainty principle, which is 2 eV-fs. This is a signature of excitation-induced dephasing (EID) caused by exciton-carrier scattering and the exciton diffraction is attributed to this mechanism. The
exciton signal has a double peak structure versus delay but this effect is not discussed in this thesis.

The continuum diffraction is due to a photon echo and has approximately the same spectrum as the excitation pulses but is shifted to lower energy by 10 meV. This energy shift is due to an enhancement of the polarizability at low energies caused by the Coulomb attraction between the photo-generated electron and hole\[53]. Although the absorption coefficient is larger at higher energy, the change in the absorption coefficient over the bandwidth of the pulse is not sufficient to explain the shift of the peak by 10 meV. The absorption coefficient increases by approximately 100% from the band edge to 60 meV above the band edge\[45] but this magnitude of increase only accounts for a peak shift of approximately 2 meV. The photon echo signal is peaked at a positive delay approximately equal to half the pulse width, which is a feature characteristic of the response for the two-pulse diffraction geometry. The diffracted power decays versus delay more rapidly at high energy, which is the cause of the distorted contours at high energy and long delay. At lower densities \(N < 2 \times 10^{16} \text{cm}^{-3}\), the continuum contribution is absent and only an exciton signal is measured. The difference in the scaling behaviour is due to the different diffraction mechanisms.

For \(\hbar\omega_0 = 1.49 \text{ eV}\), the diffracted spectrum obtained with 30 fs pulses is shown in Fig. 4.3. The diffraction is almost entirely due to a photon echo emitted from the continuum states of the HH and LH bands. A weak contribution from the exciton is evident at \(\hbar\omega_x = 1.415 \text{ eV}\) and there is a peak in the spectrum at 1.525 eV that is related to the split-off band. The dephasing rate of the continuum states is not resolved at any energy, even with 30 fs pulses. The main peak of the diffracted signal does not occur for the same energy or delay for all cuts through the diffraction surface. At low energies, the peak occurs closer to zero delay than at high energies. (Equivalently, the spectral peak occurs at low energy for early delays and high energy for long delays.) This behaviour is clearly different from that observed at \(\hbar\omega_0 = 1.46 \text{ eV}\) and is possibly due to excitation-induced dephasing of continuum states but is not investigated in this thesis.

For \(\hbar\omega_0 = 1.51 \text{ eV}\), the diffracted spectrum is shown in Fig. 4.4 and is very different from the laser spectrum. The dip in the diffracted spectrum occurs near the SO band edge, 1.52 eV. The emission is peaked at positive delay for the continuum states below
Figure 4.2: SR-FWM at $\hbar \omega_0 = 1.46$ eV and $N = 5 \times 10^{16}$ cm$^{-3}$. The delay axis of the 3d plot is 1000 fs full scale. The contour spacing, $\delta$, is 50 units for the continuum peak and 150 units for the exciton peak.
Figure 4.3: SR-FWM for $\hbar\omega_0 = 1.49$ eV and $N = 1.5 \times 10^{17}$ cm$^{-3}$. The delay axis of the 3d plot is 1000 fs full scale. The contour spacing, $\delta$, is 150 units.
Figure 4.4: SR-FWM for $\hbar \omega_0 = 1.51$ eV and $N = 1 \times 10^{17}$ cm$^{-3}$. The delay axis of the 3d plot is 500 fs full scale. The contour spacing, $\delta$, is 30 units.
1.51 eV but at zero delay above 1.51 eV. At a lower density \((N = 2 \times 10^{16} \text{ cm}^{-3})\) only the contribution above 1.51 eV exists. The asymmetry about 1.52 eV and the pronounced minimum in the spectrum are indicative of a Fano resonance at 1.52 eV. This feature is attributed to an interaction between the \(E_0 + \Delta_0\) exciton and continuum transitions of the HH and LH bands.

### 4.2 Exciton emission due to EID

In Chapter 2 a diffraction mechanism for excitons was attributed to exciton-carrier scattering and called EID. The diffracted signal is the result of a carrier density-dependent exciton dephasing rate. The spatial modulation of the total carrier density causes a spatial modulation of the exciton dephasing rate, which leads to diffraction. Signatures of the EID mechanism were identified as: (i) spectrally narrow FWM spectrum that is pulse width limited versus delay; (ii) an effect observable for parallel polarizations only. Results were presented in section 4.1 for which a large exciton contribution was evident in the SR-FWM spectrum that was attributed to EID. The arguments to support this claim are presented here.

Another example of SR-FWM is presented in Fig. 4.5, which provides a clear demonstration of the intriguing aspect of these results: the apparent violation of the uncertainty principle. The excitation energy is \(\hbar \omega_0 = 1.46\) eV and the density is \(N = 1 \times 10^{15} \text{ cm}^{-3}\). All of the diffracted power is at the exciton energy, 1.415 eV. The line width of the emission is 2 meV (full width at half maximum), which corresponds to a coherence time of 420 fs for an assumed squared Lorentzian line shape. However, no coherent interaction results in emission for a pulse separation greater than the pulse width (50 fs), which is an order of magnitude shorter than the estimate of the coherence time. This large discrepancy cannot be explained by small deviations of the line shape from a squared Lorentzian profile. Therefore, the exciton emission cannot be due to free induction decay (FID). Similar results have been reported by other researchers, for similar excitation conditions in a number of materials: bulk Ge[15, 16], InGaAs quantum wells[19], bulk GaAs[58, 20], GaAs quantum wells[21], and bulk GaAs in a magnetic field[39]. The explanations offered in these reports are either based on EID or on a coherent coupling mechanism between the
exciton and continuum states, which is distinctly different from the EID mechanism and is described by the SBE. Currently it is not clear what the relative contributions of these two mechanisms are to the exciton emission. An analysis based on numerical solution of the SBE was not attempted as part of this thesis. Instead an investigation was made of the density scaling of the diffracted power with a view to identifying a scaling behaviour characteristic for one mechanism. From the reports cited above, it is known that low excitation intensity is required to observe coherent exciton emission with a temporal response shorter than the inverse of the emission bandwidth, particularly for resonant excitation of the exciton: however, the reason(s) for this has not been explained even in terms of a simple model. In Chapter 2, a model for the diffracted power as a function of density for the EID mechanism was presented and shown to have the following functional form.

\[ J_{EID}(\tau = 0) \propto \frac{\left(\gamma_2^{-2}(N)\right)^2 N}{(\gamma_2^2 + \Gamma_2 N(0))^3} \]  

(4.1)

For a linear dependence of \( \gamma_2^{-2}(N) \) on \( N \), \( J_{EID}(\tau = 0) \) is predicted to increase as the cube of density at low density and to saturate at high density. An explicit expression for the
density dependence of the diffracted power due to the coherent coupling mechanism has not been presented in the literature, although it can be assumed that at low density it should also be cubic.

The density dependence was investigated in a low resolution SR-FWM experiment with 40 fs pulses at $\hbar\omega_0 = 1.47$ eV. The excitation energy was selected to produce a distribution of free carriers and to excite weakly the exciton transition at 1.415 eV. Weak excitation of the exciton was necessary to prevent a strong contribution from FID masking the diffraction due to EID. The exciton emission was isolated by SR-FWM detection with a resolution of 13 meV, which simply filtered out the continuum emission. The detected signal can be interpreted as $J_{EID}(\tau)$ for the exciton states. In Fig. 4.6, $J_{EID}(\tau = 0)$ is plotted versus density and has a nearly linear dependence on density. Eq. 4.1 was fitted to the data (by the least squares method) for two functional forms of $\gamma_x(N)$. The first was a linear dependence on density and the second was a square-root dependence, which was chosen as an example of a saturation behaviour that would result from a reduction of the exciton-carrier scattering cross section due to screening as density increases. The results are shown in Fig. 4.6 for both cases. Poor agreement is obtained at low density for a linear dependence but a square-root dependence provides excellent agreement at all densities. A square-root function may not be the only function which provides good agreement but it demonstrates that the simple EID model works well if the exciton dephasing rate saturates at high density. A square root function has only two fitting parameters whereas a typical saturation function $(\gamma_x^0 + \Gamma_x N/(N + N_{sat}))$ has three. Thus improved agreement with the data is not the result of additional degrees of freedom in the fitting procedure.

The exciton emission is attributed to EID based on the observed signatures of the EID effect and the scaling dependence of the diffracted power, which agrees with a simple model of EID. These results do not prove that a coherent coupling mechanism cannot explain similar observations. In fact, some of the previously cited reports observed a weaker scaling of the exciton emission compared to the continuum emission and explained the density scaling as a reduction of the exciton oscillator strength at higher density due to screening, although no quantitative analysis was presented. The effect of a reduced exciton oscillator strength was not included in the EID model presented here. Attempts to include this effect resulted in poorer agreement with the experimental results. The main conclusion is that
Figure 4.6: Diffracted power at exciton energy versus excitation density (circles) for $\hbar \omega_0 = 1.47$ eV. The solid (dashed) curve is a fit to Eq. 4.1 assuming a square root (linear) dependence of the exciton dephasing rate on density.
a simple model can explain the observed behaviour over a wide density range and that a model based on coherent coupling between exciton and continuum states is not necessary. The EID mechanism is due to an incoherent coupling of excitons and free carriers, which is certain to occur for simultaneous excitation of both excitons and free carriers. The term free carriers is used to emphasize the incoherent nature of the interaction. Continuum excitations decay into free carriers as a result of dephasing events.

4.3 LO phonon emission threshold

The dephasing rates of continuum states near the band edge were investigated by SR-FWM with 50 fs pulses tuned 40 meV above the band edge. For \( \hbar \omega_0 = 1.46 \text{ eV} \) and \( N = 5 \times 10^{16} \text{ cm}^{-3} \) the SR-FWM surface was shown in Fig. 4.2 (section 4.1) and is analyzed for the continuum states in this section. Spectral cuts through the surface at delays \( \tau = -25, 25, 100 \) fs are shown in Fig. 4.7 along with the laser spectrum. All spectra have been normalized to unity at the peak of the continuum emission for ease of comparison. The shift of the emission spectrum to lower energy than the excitation spectrum is the result of larger interband polarizability at low energy. This is due to the Coulomb interaction and is referred to as Coulomb enhancement[53]. Its effect is largest near the band edge. The main result discussed here is the distortion of the spectrum above 1.46 eV that develops at long delays. If the dephasing rate were constant over the entire energy range, the spectra would not change shape so dramatically at long delay. The interference effect of SR-FWM that was discussed in Chapter 2 is symmetric about the peak of emission but the spectra clearly become asymmetric as delay increases. The distortion is attributed to faster dephasing above 1.46 eV. The average carrier energies, \( \varepsilon_i \) (i = electron or hole), can be determined with the following expression:

\[
\varepsilon_i = (\hbar \omega_0 - E_0) \frac{m_r}{m_i}
\]

(4.2)

where \( m_i \) is the effective mass of the carrier and \( m_r \) is the reduced effective mass of the electron-hole pair. However, the effect of band gap renormalization (BGR) must be taken into account, which is estimated using the following expression[92]:

\[
\Delta E_{0,BGR} = \frac{4.64 \sqrt{Na_B^3}}{[Na_B^3 + (0.107k_B T/E_b)^2]^{1/4}E_b}
\]

(4.3)
Chapter 4. Results and Discussion

The exciton Bohr radius $a_B = 0.01 \mu m$ and the exciton binding energy $E_b = 5$ meV (see Table 2.1). The electron temperature, $k_B T$, is estimated to be $\frac{2}{3}$ of the average electron energy, which is estimated by the average electron energy without BGR. At $N = 5 \times 10^{16} \text{ cm}^{-3}$, $\Delta E_{0,BGR}$ is estimated to be 7 meV. Therefore, electrons excited from the HH band have an energy of 41 meV and the hole energies are 6 (HH) and 19 meV (LH). The LO and TO phonon energies are 41 meV and 38 meV (see Table 2.1) but TO phonon emission is symmetry forbidden for electrons near the center of the Brillouin zone ($\Gamma$ valley). The plasmon energy, $\hbar \omega_{pl}$, of the electron distribution is estimated by using the following expression[45].

$$\hbar \omega_{pl} = \hbar \sqrt{\frac{V e^2}{\epsilon_{s} m_e}}. \quad (4.1)$$

to be 8 meV at this density, which is too low to account for the increased dephasing rate at 1.46 eV. The plasmon energy of the hole distributions is smaller than 8 meV because the hole effective masses are larger than the electron effective mass. Since the holes do not have enough energy to emit TO or LO phonons, the increased dephasing rate is attributed to LO phonon emission by electrons.

From the decay of the emission versus delay, the polarization dephasing rate can be estimated. Temporal slices through the diffraction surface for $\hbar \omega_s = 1.435, 1.455, 1.475$ eV are shown in the upper part of Fig. 4.8. Clearly the decay is very rapid for all energies. It was pointed out in chapter 2 that decay constants should only be extracted from spectrally integrated measurements, since spectrally resolved results can be affected by interference effects. The SR-FWM results were numerically integrated from the band edge up to 1.46 eV and from 1.46 eV to the high energy extreme of the spectrum, to analyze the decay constants above and below the threshold energy. The results of numerical integrations are shown in the lower part of Fig. 4.8 for energies above (dashed curve) and below (solid curve) 1.46 eV. To minimize the effect of pulse width convolution, the decay constant is extracted from the data for delay $\tau > 100$ fs. For $\hbar \omega_s < 1.46$ eV, the echo decay constant is $\tau_{\text{echo}} = 30$ fs, which is close to the resolution limit with 50 fs pulses. (The rising edge has a 22 fs time constant). A line with a 30 fs decay constant is shown in the upper part of Fig. 4.8 for comparison to the SR data, which are affected slightly by interference. Since the emission is a photon echo, a 30 fs decay constant corresponds to a polarization dephasing rate of $\gamma_k = 8$ ps$^{-1}$. Since the decay constant is comparable to
Figure 4.7: Cuts through data in Fig. 4.2 at delays of -25, 25 and 100 fs. The dashed curve is the laser spectrum and the solid lines are only guides to the eye.
Chapter 4. Results and Discussion

The pulse width, a series of calculations were performed to assess the influence of the pulse width on the decay constant. The calculations were not intended to be used to extract an estimate of the dephasing rate, since the pulse shape is not known accurately. The model used for the calculations is the OBE model for a distribution of electron-hole pair states with an energy distribution quadratic in the wave vector \( k \). Calculations were performed for 1000 points in \( k \)-space from zero to 500 \( \mu \text{m}^{-1} \) over a temporal range of 1 ps with a 1 fs step size. The temporal profile of the pulse was assumed to be \( E(t) = \text{sech}(1.76t/\tau_p) \), where \( \tau_p \) is the pulse width measured at full width at half maximum of the intensity. The pulse width and dephasing rate were varied to optimize agreement with the experimental results. By visual inspection, the optimal parameters were determined to be \( \tau_p = 55 \pm 5 \) fs and \( \gamma_k = 12 \pm 2 \) ps\(^{-1} \). The numerical results indicate that the 30 fs decay constant may be slightly affected by the pulse width. The decay constant for the trace above 1.46 eV is not resolved from the pulse profile and it is not possible to estimate a phonon emission rate directly from a comparison of the dephasing rates above and below the threshold energy. This is mainly due to the noise level rather than the bandwidth of the pulses; at \( \tau = 100 \) fs the signal is roughly at the noise level.

The value of the phonon emission rate is not the most important result. More important is the fact that the threshold feature demonstrates that the dephasing rate below 1.46 eV is resolved. The 30 fs decay constant cannot be entirely ascribed to an artifact of the pulse shape and/or convolution effects. The continuum dephasing rate is therefore at least 8 ps\(^{-1} \) below the threshold for LO phonon emission by electrons and at a carrier density of \( N = 5 \times 10^{16} \text{ cm}^{-3} \). Dephasing rates for continuum excitations in bulk GaAs have been reported at similar excess energy and carrier density. Wehner et al. measured a continuum dephasing rate of 20 ps\(^{-1} \) in GaAs by FWM with 15 fs pulses\(^{[58]} \). In two other reports, continuum dephasing rates of 5 ps\(^{-1} \) were measured with 100 fs pulses\(^{[25, 17]} \). At much higher photon energy and higher carrier density than the experiments reported here, the continuum dephasing rate in bulk GaAs was measured by FWM with 6 fs pulses to be 25–50 ps\(^{-1} \)\(^{[11]} \) and to be a function of carrier density. Continuum dephasing rates have also been measured in quantum well structures\(^{[24]} \) and modulation-doped quantum wells\(^{[23]} \). None of the reports cited above estimated the effect of pulse width on the the continuum dephasing rate determined from the decay of a FWM signal as a function of delay. The
Figure 4.8: Upper graph: Cuts through data in Fig. 4.2 at three values of $\hbar \omega_s$. Lower graph: numerically integrated SR-FWM data for an energy range below 1.46 eV and above 1.46 eV.
Chapter 4. Results and Discussion

dephasing rate reported here is slightly lower than typically measured in bulk GaAs and this is the first report where the LO phonon emission threshold is observed in spectrally resolved FWM.

Since the dephasing rate above the LO phonon emission threshold was not resolved with 50 fs pulses and SR-FWM detection, an attempt was made to resolve the decay with shorter pulses tuned to higher energy. SI-FWM experiments were performed at $\hbar \omega_0 = 1.51$ eV with perpendicularly polarized 30-fs pulses at a density $N = 8 \times 10^{16}$ cm$^{-3}$. (The continuum states in this energy range must be investigated with perpendicularly polarized pulses. to avoid effects related to the split-off exciton. These effects are discussed in section 4.4.) A SR-FWM experiment was performed to ensure that the contribution of the split-off exciton was negligible. At a lower density of $3 \times 10^{16}$ cm$^{-3}$, the SR-FWM experiment did not determine the energy of the emission due to noise limitations and therefore the contribution of the split-off exciton cannot be regarded as negligible at $N = 3 \times 10^{16}$ cm$^{-3}$. Only SI-FWM results for $N = 8 \times 10^{16}$ cm$^{-3}$, which are shown in the lower part of Fig. 4.3 as circles, are discussed here. The decay constant of the SI-FWM trace is 20 fs but the dephasing rate is probably greater than 13 ps$^{-1}$ due to the effect of convolution with the pulse profile. Therefore, the LO phonon emission rate is estimated to be at least 5 ps$^{-1}$. The LO phonon emission rate is calculated to be 10 ps$^{-1}$ using the following expression[2]:

$$W_{em}^{\text{e,LO}} = \frac{e^2 \sqrt{2m_e \hbar \omega_{LO}}}{4\pi\varepsilon_0 \hbar^2} \left( \frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_s} \right).$$  \hspace{1cm} (4.5)

The LO phonon emission rate has been measured in InP by photoemission experiments and was estimated to be in the range 14–20 ps$^{-1}$[93].

Some simple calculations were performed to understand the effect of an increased dephasing rate at a threshold energy on the interference observed in SR-FWM. In chapter 2, results of a calculation of the SR-FWM traces for five energies were presented for which the dephasing rate was independent of energy. The results shown in Fig. 4.9 are for a dephasing rate of 10 ps$^{-1}$ below 1.46 eV and 50 ps$^{-1}$ above 1.46 eV. The main result is that the magnitudes of the spectral components are asymmetric about the spectral peak. The interference effect discussed in chapter 2 is much less pronounced and the decay is faster on the high energy side, as expected; however, the difference between the decay constants for energies above 1.46 eV and below 1.46 eV is smaller than the difference in dephasing
Figure 4.9: Calculated spectrally resolved emission with parameters: photon energy is 1.46 eV, 50 fs pulse width, and 10 ps$^{-1}$ dephasing rate below 1.46 eV and 50 ps$^{-1}$ above 1.46 eV. Results are shown for five energies relative to the peak of the laser spectrum: 0 meV (solid line); +10 meV (solid square), -10 meV (hollow square), +20 meV (solid circle), -20 meV (hollow circle).

...rates. The calculations are in qualitative agreement with the experimental results but an unrealistically high phonon emission rate (40 ps$^{-1}$) was necessary to produce even the slight difference between the decay constants for energies above and below 1.46 eV that is evident in Fig. 4.9. This is likely due to the assumed temporal shape of the pulses, which was $E(t) = \text{sech}(1.76t/\tau_p)$. The effect of the energy dependent dephasing rate is more evident in the magnitude than in the decay of each spectral component.
4.4 Coherent response at the $E_0 + \Delta_0$ band edge

The coherent response near the $E_0 + \Delta_0$ transition was investigated by performing SR-FWM experiments with 30–40 fs pulses tuned to $\hbar \omega_0 = 1.52$ eV. Experiments were performed over a density range from $N = 1 \times 10^{16}$ cm$^{-3}$ to $1.5 \times 10^{17}$ cm$^{-3}$, limited by noise at the lowest density. FWM spectra are presented for parallel ($\parallel$SR) and perpendicular ($\perp$SR) orientations of the electric field polarization vectors. The cross-polarized case was obtained by rotating a half-wave plate in one beam. The limited bandwidth of the half-wave plate implies that the polarization of the rotated beam is not exactly linear over the full bandwidth of the pulse. The polarization state of the rotated beam was characterized and was discussed in chapter 3. For $\hbar \omega_0 = 1.52$ eV, the ratio of power in the orthogonally polarized directions was 5:1 at the peak of the laser spectrum. Although the polarizations were not exactly perpendicular, the terms perpendicular and cross-polarized are used to distinguish this excitation condition from the co-polarized case. The conclusions drawn in this section regarding emission from the split-off band are based on data obtained over the full range of density. The data for each density are described separately before arguments are made about the interpretation of the data.

The $\parallel$SR for $N = 1 \times 10^{16}$ cm$^{-3}$ obtained with 36 fs pulses is shown in Fig. 4.10(a) and is centered at $\hbar \omega_s = 1.525$ eV, which is near $E_0 + \Delta_0$. The response versus delay is pulse-width limited and shorter than the inverse of the emission bandwidth. For this reason the emission cannot be attributed solely to the continuum states. The line shape is asymmetric, as can be seen in Fig. 4.10(b), which shows a cut through the diffraction surface at zero delay. The low energy side of the peak is steeper than the high energy side. No emission was detected at any energy in the $\perp$SR at this density.

At higher density, the emission is stronger and has a spectrum similar to the low density case for $\hbar \omega_s > 1.515$ eV. Fig. 4.11(a) shows the $\parallel$SR for $N = 7 \times 10^{16}$ cm$^{-3}$ obtained with 38 fs pulses. There is also a strong contribution centered at $\hbar \omega_s = 1.49$ eV and $\tau = 15$ fs due to a photon echo from the continuum transitions of the HH and LH bands, which was discussed in section 4.3. There is a distinct minimum in the $\parallel$SR spectrum at $\hbar \omega_s = 1.515$ eV, which is clearly evident in the spectral cut at zero delay shown in Fig. 4.11(b). The $\perp$SR is not shown for this density but is similar to the high density case.
Figure 4.10: (a) Contour plot of coherent emission for $\|\text{SR-FWM}$ at $N = 1 \times 10^{16} \text{cm}^{-3}$ for $\hbar \omega_0 = 1.52 \text{ eV}$. The contour spacing, $\delta$, is 5 units and the lowest contour is at 5 units. Unit size is arbitrary. (b) Diffracted spectrum at zero delay.
Figure 4.11: (a) Contour plot of coherent emission for $||$SR-FWM at $N = 7 \times 10^{16}$ cm$^{-3}$ for $\hbar \omega_0 = 1.52$ eV. The contour spacing, $\delta$, is 10 units and the lowest contour is at 10 units. Unit size is arbitrary. (b) Diffracted spectrum at zero delay. The laser spectrum is also shown (dashed curve).
discussed next.

For the highest density, \( N = 1.5 \times 10^{17} \text{ cm}^{-3} \), contour plots of \( ||SR \) and \( \perp SR \) obtained with 38 fs pulses are shown in Fig. 4.12. The \( ||SR \) is again comprised of two contributions, which are referred to as the echo and \( E_0 + \Delta_0 \) contributions. The echo contribution at \( \hbar \omega_s = 1.49 \text{ eV} \) is stronger than the \( E_0 + \Delta_0 \) contribution. The \( \perp SR \) shows only a weak contribution near \( E_0 + \Delta_0 \) and is comprised of primarily the HH and LH echo contribution. A weak peak at 1.525 eV exists possibly because the polarizations are not perfectly perpendicular at all energies in the bandwidth of the pulse. Cuts through the contours at zero delay are shown in Fig. 4.13 for both orientations. The minimum in the \( ||SR \) spectrum is at 1.515 eV but its value is not exactly zero.

The general features observed for all densities are: (i) the \( E_0 + \Delta_0 \) contribution is much more prominent for \( ||SR \) than \( \perp SR \) and is peaked at \( \tau = 0 \); (ii) the spectral width of the \( E_0 + \Delta_0 \) contribution is narrower than the pulse bandwidth yet the response is pulse-width limited versus delay; (iii) the \( ||SR \) has a minimum at \( \hbar \omega_s = 1.515 \text{ eV} \), except at the lowest density. The energies of the minimum and the peak near \( E_0 + \Delta_0 \) do not shift as the laser is tuned. The echo contribution is similar to that observed for \( \hbar \omega_0 = 1.46 \) and 1.49 eV. The \( \perp SR \) at high and medium densities (not observed at low density) has only a small contribution from the split-off band and is therefore primarily attributed to a photon echo from the continuum excitations of the HH and LH bands. However, the contribution of the split-off band to the \( ||SR \) does not simply add power to the diffracted spectrum. A comparison of \( ||SR \) and \( \perp SR \) reveals that the \( ||SR \) emission at \( \hbar \omega_s = 1.515 \text{ eV} \) is reduced while the emission at \( \hbar \omega_s = 1.525 \text{ eV} \) is enhanced relative to \( \perp SR \). The observed minimum in the \( ||SR\text{-FWM} \) spectrum is surprising, since the linear absorption spectrum (shown in Fig. 4.1) does not exhibit such a minimum near \( E_0 + \Delta_0 \). Previous investigations of SR-FWM from continuum transitions in GaAs that are far removed from the \( E_0 + \Delta_0 \) transition [25, 17] have reported FWM spectra that reflect the general shape of the laser spectra. Since the results reported here are the first investigation of the ultrafast coherent response at the \( E_0 + \Delta_0 \) transition of a III-V semiconductor, the main objective is to identify a physical mechanism that can explain the observed minimum in the spectral profile of the \( ||SR \) coherent emission. Two mechanisms were identified as possible candidates to explain the observations: excitation-induced dephasing (EID) of the split-off exciton
Figure 4.12: Contour plots of the coherent emission for (a) parallel and (b) perpendicular configuration of polarizations at $N = 1.5 \times 10^{17}$ cm$^{-3}$ for $\hbar \omega_0 = 1.52$ eV. The contours levels start at 50 units and are spaced by 50 units. Unit size is arbitrary.
Figure 4.13: Spectra of the coherent emission at delay $\tau = 0$ fs for (a) parallel and (b) perpendicular polarization orientations. Density is $N = 1.5 \times 10^{17}$ cm$^{-3}$ for $\hbar \omega_0 = 1.52$ eV. The dashed curve in (b) is the laser spectrum. The spectra are cuts through the surfaces shown in Fig. 4.12.
due to exciton-carrier scattering, and Fano interference between the split-off exciton and continuum excitations of the HH and/or LH bands. Both of these mechanisms are discussed in the following section, where a discussion of the EID mechanism precedes the discussion of Fano interference.

It has been pointed out that a difference between FWM signals for parallel and perpendicular orientations can be explained by EID[67, 20, 19], which was discussed with respect to the fundamental exciton in section 4.2. The coherent response near \( E_0 + \Delta_0 \) exhibits three features that are indicative of EID: a spectral width narrower than the pulse bandwidth and a temporal response that is pulse-width limited versus delay, maximum emission at zero delay, and a strong polarization dependence. The main difference between the observations for the \( E_0 + \Delta_0 \) exciton and the fundamental exciton is the destructive interference observed near \( E_0 + \Delta_0 \). An incoherent EID process could produce \( E_0 + \Delta_0 \) exciton emission that is out of phase with the echo contribution from the HH and LH bands. The two contributions would interfere destructively if they were out of phase and could lead to a spectral profile similar to the observations for parallel polarized pulses.

Since the EID mechanism only produces a contribution for parallel polarized pulses there would be no interference in the perpendicular case. The phase of emission due to EID is determined by the density dependence of the dephasing rate. A decreasing dephasing rate with increasing density causes the EID contribution to be out of phase with the echo contribution. Screening of the split-off hole phonon interactions could cause the \( E_0 + \Delta_0 \) exciton dephasing rate to decrease as density increases. However, at the lowest density \( (N = 1 \times 10^{16} \text{cm}^{-3}) \), only the exciton emission above 1.515 eV is detectable. Therefore, the asymmetric line shape cannot be the result of interference between an exciton polarization and a continuum polarization, since the continuum contribution is very weak.

Additionally, screening of the hole-phonon interactions would cause the line width of the \( E_0 + \Delta_0 \) exciton to decrease as density increases which does not agree with the observed broadening of the emission as density increases. Although EID may affect the emission spectrum by enhancing the emission from states with long dephasing times (i.e. the \( E_0 + \Delta_0 \) exciton), EID cannot explain the spectral shape at all densities.

The total diffracted power was determined by numerical integration of the spectra (at zero delay) and is the same for both \( \parallel \text{SR} \) and \( \parallel \text{SR} \) at densities above \( 7 \times 10^{16} \text{cm}^{-3} \). This
suggests that the difference between \( \perp \text{SR} \) and \( \parallel \text{SR} \) is due to a redistribution of oscillator strength as opposed to an introduction of an additional source of emission. The spectral profile of \( \parallel \text{SR} \) near \( E_0 + \Delta_0 \) is indicative of a Fano resonance, since there are both destructive interference and constructive interference regions in the spectra. An interaction between the discrete \( E_0 + \Delta_0 \) exciton and the optically coupled HH and LH continuum states could give rise to such a Fano profile.

In order to assess the plausibility of the Fano interference interpretation, the \( \parallel \text{SR} \) data are compared to the predictions of the model that was presented in chapter 2 for the FWM spectrum from a Fano resonance[68]. In order to compare experimental results directly with this model, the data must be normalized by the FWM spectrum of the continuum states without any coupling to the \( E_0 + \Delta_0 \) exciton. Since the \( \perp \text{SR} \) spectra are only weakly affected by the \( E_0 + \Delta_0 \) resonance, these are used as normalization spectra. Since no signal was detected for \( \perp \text{SR} \) at the lowest density, a normalization spectrum was assumed to be given by a Gaussian spectrum centered at \( h \omega_s = 1.49 \text{ eV} \) with a full width at half maximum of 41.5 meV. The parameters which provided the best fit of the model to the normalized spectra were determined at zero delay for \( N = 1 \times 10^{16} \text{ cm}^{-3}, 8 \times 10^{16} \text{ cm}^{-3} \) and \( 1.5 \times 10^{17} \text{ cm}^{-3} \). There are two methods to calculate the best fitting parameters for normalized data. If the \( \parallel \text{SR} \) data are divided by the \( \perp \text{SR} \) data at \( \tau = 0 \text{ fs} \), large uncertainties are introduced at the extremes of the normalized spectra because the diffracted spectra are weak at the extremes. Therefore to perform a best fit procedure, each data point must be weighted by the uncertainty. which will be different for each data point. This procedure minimizes the sum

\[
\sum_i \left[ \frac{1}{\sigma_i} \left( \frac{\parallel \text{SR}_i}{\perp \text{SR}_i} - f(x_i) \right) \right]^2 \tag{4.6}
\]

where \( i \) labels the data points. \( \sigma_i \) is the uncertainty, and \( f(x_i) \) is the function that contains the parameters to be varied (Eq. 2.64). This weighting procedure can be avoided by minimizing the sum

\[
\sum_i \left[ \frac{1}{\sigma_i} \left( \parallel \text{SR}_i - \perp \text{SR}_i f(x_i) \right) \right]^2 \tag{4.7}
\]

since all the uncertainties are approximately equal in this case. The results of calculations using the model of FWM from a Fano resonance, with parameters obtained by minimizing Eq. 4.7 for three densities, are presented in Figs. 4.14(a) (\( N = 1.5 \times 10^{17} \text{ cm}^{-3} \)), 4.15(a)
Chapter 4. Results and Discussion

Table 4.1: Parameters obtained by least squares fits of the model of FWM at a Fano resonance to experimental data. The parameters $q'$ and $\Gamma_F$ are defined in the text.

<table>
<thead>
<tr>
<th>Density</th>
<th>$q'$ (eV)$^{1/2}$</th>
<th>$\Gamma_F/2$ (eV)</th>
<th>$\varepsilon_x$ (eV)</th>
<th>$q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{16}$ cm$^{-3}$</td>
<td>0.098</td>
<td>0.0060</td>
<td>1.524</td>
<td>1.27</td>
</tr>
<tr>
<td>$8 \times 10^{16}$ cm$^{-3}$</td>
<td>0.041</td>
<td>0.0024</td>
<td>1.520</td>
<td>0.84</td>
</tr>
<tr>
<td>$1.5 \times 10^{17}$ cm$^{-3}$</td>
<td>0.021</td>
<td>0.0021</td>
<td>1.520</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The increase in the normalized $\|\text{SR}$ at low energy is not understood completely but could be due to EID of the continuum states.

The results of the fitting procedure indicate that the model can account for the main features of the data which are the minimum at 1.515 eV and the peak above 1.52 eV, which are both clearly evident for the two highest densities. At the lowest density, the asymmetric shape of the emission spectrum can also be described by the model. At the two highest densities, the calculations underestimate the width of the peak at $E_0 + \Delta_0$, which may be an indication that $V_F$ is not constant over the entire energy interval as was assumed in the model. The Fano FWM line shape is characterized by three parameters, which are the inverse lifetime of the discrete state due to interaction with the continuum, $\Gamma_F = 2\pi g V_F^2/\hbar$ ($g$ is the continuum density of states and $V_F$ is the interaction matrix element), the ratio of transition amplitudes for the discrete state and the continuum, $q' = \mu_\varepsilon/\mu_\varepsilon \sqrt{\pi g}$, and the energy of the discrete state, $\varepsilon_x$. The Fano parameter $q = q'/\sqrt{\Gamma_F/2}$ was defined in Eq. 2.58. The parameters $\Gamma_F/2, q'$ and $\varepsilon_x$ were obtained by a least squares fit to the data for each density and are tabulated in Table 4.1. Although there is no explicit density dependence...
Figure 4.14: (a) FWM spectra at delay $\tau = 0$ and $N = 1.5 \times 10^{17} \text{ cm}^{-3}$ for parallel (circles) and perpendicular (squares) polarization configurations (these are the same data as presented in Fig. 4.13). The solid curve is the best fit of the model of FWM at a Fano resonance to the $\parallel$SR data using the $\perp$SR data as a normalization spectrum. (b) The $\parallel$SR spectrum normalized by the $\perp$SR spectrum (circles) and the same best fit curve as discussed for (a).
and the same best fit curve as discussed for (a).

The \( |S_R| \) spectrum normalized by the TGR spectrum (circles) of the model of PVM at a Fano resonance to the TGR data using the TGR data as a reference. The solid curve is the best fit and perpendicular (squares) polarization configurations. The solid curve is the best fit.

**Figure 4.15:** (a) PVM spectra at delay \( t = 0 \) and \( N = 8 \times 10^{-6} \) cm\(^{-2}\) for parallel (circles)
Figure 4.16: FWM spectra at delay $\tau = 0$ and $N = 1 \times 10^{16}$ cm$^{-3}$ for parallel polarization configuration. The solid curve is the best fit of the model of FWM at a Fano resonance to the ||SR data using a Gaussian centered at 1.49 eV with a full width a half maximum of 41.5 meV as a normalization spectrum.
in the Fano model, the FWM spectra are characterized by $q$, which can be taken to be an adjustable parameter. The results of fits to the model (see Table 4.1) indicate that $q$ decreases as density increases and that this is due to a combination of both $q'$ and $\Gamma_F$ decreasing as density increases. The split-off exciton dipole moment is expected to decrease as density increases due to screening of the Coulomb interaction by free carriers, which may explain the density dependence of $q'$. However, the agreement between the calculations and the experimental results is not good enough to draw a conclusion about the density scaling of either $q'$ or $\Gamma_F$ independently. The numerical results obtained by fitting the model to the data must be interpreted within the following context. The normalization spectra used to obtain a direct comparison to the model were the $\perp$SR spectra (except at the lowest density) because the $\perp$SR appeared to be only weakly affected by the $E_0 + \Delta_0$ transition. However, it has not been proven that the $\perp$SR exhibit no Fano interference effects. In fact, the $\perp$SR at zero delay do have a small feature at $E_0 + \Delta_0$ but the fitting parameters are not very sensitive to its presence. The value obtained for $\Gamma_F$ at $N = 8 \times 10^{16} \text{cm}^{-3}$ increased by approximately 20% when the $\perp$SR spectrum was smoothed out near $E_0 + \Delta_0$.

To characterize further the experimental observations, the density dependence of certain features of the $\parallel$SR spectra are noted. In order to identify trends as a function of density, data sets for which the laser spectrum, pulse width, and spot size were identical are compared. The extent to which small changes in these variables affect the following observations is difficult to assess. The trends observed in the $\parallel$SR spectra at zero delay as density increases are: (i) the magnitude of the $E_0 + \Delta_0$ contribution relative to the echo contribution decreases; (ii) the spectral width of the $E_0 + \Delta_0$ contribution increases; (iii) the energy of the peak near $E_0 + \Delta_0$ shifts to slightly higher energy; (iv) the minimum value in the $\parallel$SR at $\hbar\omega_s = 1.515 \text{ eV}$ increases slightly but does not shift in energy above $N = 7 \times 10^{16} \text{ cm}^{-3}$ (at the lowest density, a minimum is not clearly evident). The most important observation is item (i) because it is the least subtle of the observed trends. Fig. 4.17 shows the spectral position and width of the $E_0 + \Delta_0$ contribution as a function of density for three data sets. The data points that are connected by lines can be directly compared but the excitation conditions (spectrum, pulse width, spot size) were not identical for the different sets.

The results of SI-FWM measurements provide additional evidence for the presence of a
Figure 4.17: A summary of the general features of the $E_0 + \Delta_0$ contribution to the $||$SR diffracted spectra at $r = 0$ observed as a function of density. Three data sets are presented and are distinguished by the symbol (circle, square, or triangle). The spectral width is the full width at half maximum and the spectral position is the peak of the emission spectrum near $E_0 + \Delta_0$. 

Chaprer 4. Results and Discussion
Chapter 4. Results and Discussion

Fano resonance. In Fig. 4.18 are shown the SI-FWM data obtained at \( N = 8 \times 10^{16} \text{ cm}^{-3} \) with 31 fs pulses for parallel (dashed line) and perpendicular (solid line) configurations of the electric field polarization vectors. The SI-FWM trace for parallel polarizations has a partial oscillation versus delay (the diffracted power dips at approximately 70 fs delay), which is the predicted behaviour for the response of a Fano resonance in the limit of small \( q \). For perpendicular polarizations, the SI-FWM trace decays exponentially with a time constant of 20 fs. Thus an indication of a Fano interference effect is only observed for parallel polarized pulses as is the case for SR-FWM results. For large \( q \), Meier et al. [68] showed that the dip is predicted to vanish. The SR-FWM results indicate that \( q \) decreases as density increases, which implies that the dip observed in the SI-FWM trace at positive delay (see Fig. 4.18) should be less pronounced at lower density [68]. Fig. 4.19 shows the SI traces for \( N = 8 \times 10^{16} \text{ cm}^{-3} \) and \( 2 \times 10^{16} \text{ cm}^{-3} \) normalized to unity at the peaks. The contrast between the traces is quite small but the dip in the low density trace at 70 fs is less pronounced than for the high density trace. The differences between the traces in the rising edge is due to the fact that at low density the \( E_0 + \Delta_0 \) contribution, which peaks at zero delay, is stronger relative to the echo contribution, which peaks at positive delay and determines the decay of the SI trace. Meier et al. pointed out that the prediction of a dip in the SI-FWM trace was obtained by numerical calculation as opposed to being an analytic result. Therefore, the characteristics of the dip cannot be compared to the model by fitting a parameter. The SI results are not conclusive about the density scaling of \( q \) but they are consistent with the SR results and the predictions of the model discussed by Meier et al.

In summary, the results indicate that the observed spectral profile of the SI-FWM can be explained by a model based on Fano interference. The SI-FWM spectra exhibit an asymmetric line shape in an energy range where a discrete state (the \( E_0 + \Delta_0 \) exciton) is energetically degenerate with a continuum of transitions (HH and LH transitions). The Fano interference model is based on the reasonable assumption that an interaction between \( E_0 + \Delta_0 \) excitons and continuum excitations of the HH and LH bands exists. The predictions of a model of FWM from a Fano resonance agree with the main features of the observed spectra at all densities and indicate that the Fano coupling parameter \( q \) decreases as density increases. The main features referred to are the minimum in the spectra at \( \hbar \omega_1 = \)
Figure 4.18: SI-FWM traces versus delay at $8 \times 10^{16} \text{ cm}^{-3}$ obtained with 31 fs pulses for parallel (dashed curve) and perpendicular (solid curve) polarizations.
Figure 4.19: SI-FWM traces versus delay obtained with 31 fs, parallel polarized pulses at $8 \times 10^{16} \text{ cm}^{-3}$ (dashed curve) and $2 \times 10^{16} \text{ cm}^{-3}$ (solid curve).
1.515 eV, the peak near \(E_0 + \Delta_0\), and the reduction of the amplitude of the \(E_0 + \Delta_0\) contribution relative to the echo contribution as density increases. The inverse lifetime of the split-off exciton due to an interaction with the HH and LH continua is determined to be approximately 5 meV in the density range \(1 \times 10^{16} \text{ cm}^{-3}\) to \(1 \times 10^{17} \text{ cm}^{-3}\). The Fano interference model also agrees with the observed behaviour of the SI-FWM trace as a function of delay. An extension of the model to allow an energy dependent interaction matrix element may improve the agreement with the SR-FWM data and explain the more subtle aspects of the observations (which are the shift of the peak of the \(E_0 + \Delta_0\) contribution to higher energy, and the broadening of the \(E_0 + \Delta_0\) contribution as density increases). The SR-FWM results obtained at low density confirm that a mechanism based on interference between two contributions to the emission cannot explain the observed SR spectral profile.

The SR-FWM results clearly indicate that observation of Fano interference features are dependent upon the polarizations of the optical pulses. The FWM model presented by Meier et al. [68] does not account for differently polarized pulses. A simple model of FWM for both parallel and perpendicularly polarized pulses was discussed in chapter 2. It was shown that the FWM spectrum can be different for the two polarization configurations provided the interaction matrix elements satisfy a certain condition. However, the model does not predict that the Fano interference effects are absent in the perpendicular case. The FWM spectrum predicted by the simple model for parallel polarized pulses is different from that predicted by the model of Meier et al., which is essentially a linear Fano absorption profile. Agreement with the experimental results is better for the linear Fano profile than for the spectrum predicted by the simplified model. The polarization dependence is not understood at present, but was utilized to provide normalization spectra that allowed an analysis of the Fano interference mechanism. In light of the fact that the polarization effects are not understood, the interaction mechanism has not been identified.

The Coulomb interaction has been shown to couple excitons to continuum excitations of different bands[29] and to lead to Fano interference that was observed in linear absorption measurements of bulk GaAs in a magnetic field[34] and a quantum well structure[32]. Therefore, the Coulomb interaction is an excellent candidate. However, some theoretical work is required to analyze the polarization dependence of the interaction as observed by FWM. A description of coherent electron dynamics that includes the Coulomb interaction.
Chapter 4. Results and Discussion

is given by the semiconductor Bloch equations (SBE). A two-band model of the SBE is known to be inadequate to describe effects sensitive to the electric field polarizations[60, 64]. A multiple band model that accounts for the crystal structure is necessary[65]. A theory that includes the split-off band has not been presented in the literature but, in principle, including the split-off band is a simple extension of models that include light and heavy hole bands[65]. It has been shown that the FWM selection rules are not changed within the approximations of the SBE[66]. The Fano interference effect could result from an interband coupling of exciton and continuum states, as was demonstrated for inter-subband coupling in quantum wells[29].

In addition, the interference is only observed in the nonlinear response and not in the sample transmission spectrum (Fig. 4.1 shows no indication of an interference effect near \( E_0 + \Delta_0 \)). Therefore, the interaction may be due to a density dependent mechanism such as exciton-exciton scattering. The observed density dependence of the Fano coupling parameter \( q \) is consistent with this interpretation. It should be pointed out that the absorption spectrum of GaAs near \( E_0 + \Delta_0 \) does not exhibit Fano interference either[35].

This chapter closes with a discussion of two related observations that have been reported in the literature. The \( E_0 \) exciton dephasing rate has been shown to be dependent upon polarization configuration for some quantum well samples[64]. Those results were explained by an inhomogeneous broadening due to well width fluctuations, which leads to different temporal dynamics for parallel or perpendicular configurations. The Fano profile reported in this thesis is observed at zero temporal delay and therefore is not likely to be explained by a similar theory as used to explain the results discussed in Ref. [64].

It has been shown that the contributions of terms neglected by the approximations used to derive the SBE (called the collision terms of the Coulomb interaction) produce FWM spectra for \\( \perp \) SR and \\( \parallel \) SR with different spectral profiles[16]. These contributions represent scattering of a polarization from a polarization grating as opposed to a population grating, which is the basis of the diffraction mechanisms discussed in chapter 2. The calculations reported in Ref. [16] were specific to the \( E_0 \) exciton and did not address the \( E_0 + \Delta_0 \) exciton but did demonstrate that the coupling between continuum states and the \( E_0 \) exciton could be polarization sensitive. To date a tractable theory has not been presented that allows a simple calculation of these effects. It is possible that scattering contributions that stem
from the interaction of three coherent polarizations (referred to as polarization scattering in Ref. [16]) may explain the interference phenomena reported in this thesis.

In summary of the results presented in this section, the $E_0 + \Delta_0$ exciton was spectrally resolved in the coherent emission spectrum for parallel polarized excitation pulses and shown to have a Fano-like spectral profile. Qualitative agreement between the experimental results and the predictions of a model of FWM at Fano resonances was provided as support for the claim that the spectral profile is indeed due to an interaction between the $E_0 + \Delta_0$ exciton and HH and LH continuum transitions. Unexpectedly, observation of the Fano-like profile is dependent upon polarization orientation. Possible explanations were discussed.
Chapter 5

Conclusions

The coherent electronic response of InP at 5 K has been investigated over a 140 meV range above the band gap, using the spectrally resolved four-wave mixing technique with 30–50 fs pulses. Interactions between excitons and continuum excitations were investigated for both the $E_0$ exciton and the $E_0 + \Delta_0$ exciton. This chapter is a summary of the experimental results and conclusions.

For excitation near the $E_0$ band gap, $E_0$ excitons were excited simultaneously with a large bandwidth of continuum excitations. The diffracted coherent emission from $E_0$ excitons was shown to exhibit markedly different behaviour as a function of delay than expected of free induction decay. Although the emission was spectrally narrower than the pulse bandwidth, no coherent interaction between the optical pulses resulted in diffraction for pulse separations greater than the pulse width. i.e. the temporal response was pulse-width limited versus delay. The dependence of the total energy diffracted by excitons on excitation density was shown to be nearly linear from $1 \times 10^{15}$ cm$^{-3}$ to $5 \times 10^{16}$ cm$^{-3}$. which is significantly different from the cubic dependence expected of free induction decay. Interactions between $E_0$ excitons and free carriers were shown to provide the dominant source of diffraction. This diffraction mechanism is called excitation-induced dephasing and is due to incoherent scattering of $E_0$ excitons by free carriers. A simple model of coherent exciton dynamics and a square-root dependence of the exciton dephasing rate on carrier density were shown to explain the results over a wide density range. The square-root density dependence was interpreted as an indication that the exciton-carrier scattering cross section decreases as density increases. Similar results for different semiconductors have been reported and interpreted as exciton-continuum coupling by other researchers. It has been suggested that exciton-continuum coupling constitutes a new contribution to the coherent response of semiconductors[19]. However, the EID mechanism is based on
exciton-carrier scattering, which has been known to affect exciton dephasing since the work of Schultheis et al. [12]. In the context of simultaneous exciton and continuum excitation, the EID mechanism can be considered a new contribution to the diffracted emission but not a new contribution to the coherent response of excitons. The results of this thesis suggest that a simple interpretation may be applicable to the results obtained by others.

The coherent dynamics of continuum excitations associated with the light and heavy hole valence bands were investigated from the band edge up to 140 meV above the band gap. The continuum dephasing rate increases abruptly at the threshold energy for LO phonon emission by electrons. Below this threshold energy, the dephasing rate was determined to be at least 8 ps\(^{-1}\) at a density of 5 \times 10^{16} \text{cm}^{-3} with 50 fs pulses. Above the threshold energy, the dephasing rate was not resolved at this density with 50 fs pulses. By using perpendicularly polarized 30 fs pulses and spectrally integrated detection, the dephasing rate was estimated to be at least 13 ps\(^{-1}\) for the continuum states above the phonon emission threshold. This is the first report of an increased continuum dephasing rate above a threshold energy.

The coherent response near \(E_0 + \Delta_0\) was investigated with 30–40 fs pulses by SR-FWM and SI-FWM. The \(E_0 + \Delta_0\) exciton was spectrally resolved in the coherent emission obtained with co-polarized excitation pulses and found to have a very different line shape compared to that of the \(E_0\) exciton. The coherent emission spectrum has a Fano-like line shape near \(E_0 + \Delta_0\), with a distinct minimum at 1.515 eV and a peak at 1.525 eV. As a function of delay the SI-FWM trace has a non-exponential decay that exhibits a dip at positive delay. The results were discussed in terms of coupled exciton-continuum excitations that exist due to an interaction between \(E_0 + \Delta_0\) excitons and continuum excitations of heavy and light hole bands. A comparison was made between the data and the predictions of a model of FWM from a Fano resonance to support the claim that Fano interference is an excellent candidate to explain the observations. The model describes reasonably accurately the main features of the SR-FWM data at all densities in the range \(1 \times 10^{16} \text{cm}^{-3}\) to \(1.5 \times 10^{17} \text{cm}^{-3}\). The discrepancies between the model and the data could possibly be resolved by allowing the interaction matrix element between \(E_0 + \Delta_0\) exciton and continuum states to be dependent on energy. The predictions of the model are also in qualitative agreement with the SI results; this conclusion is drawn.
from a comparison to published calculations rather than to calculations performed as part of this thesis. The results obtained by fitting the model to the SR-FWM data indicate that the Fano coupling parameter \( q \) decreases as density increases. However, the results are inconclusive about whether the decrease of \( q \) is due to an increase of the interaction strength or a decrease of the \( E_0 + \Delta_0 \) exciton oscillator strength. An improved model (possibly with an energy dependent interaction matrix element) may allow a determination of the density dependence of the interaction strength, which was determined to be approximately 5 meV in the density range investigated. Therefore, the lifetime of \( E_0 + \Delta_0 \) excitons due to decay to the optically coupled continuum states of the HH and LH bands is determined to be approximately 130 fs.

Experiments were performed for both parallel and perpendicular configurations of the electric field polarization vectors. The Fano-like spectral profile and the non-exponential decay of the SI-FWM trace versus delay were much more prominent for the parallel configuration, which suggests that the exciton-continuum interaction is dependent upon polarization configuration. The interaction mechanism has not been identified since the origin of the polarization dependence is not understood at present. The Coulomb interaction has been shown to couple exciton and continuum states in quantum wells and in a bulk semiconductor in a magnetic field and may be the coupling mechanism. The most comprehensive theoretical approach used for analyzing FWM experiments is the model of the semiconductor Bloch equations. A calculation based on this model that includes all three valence bands and the appropriate coupling between the valence bands would be very useful for assessing the role of the Coulomb interaction in the Fano-like interference phenomena. Rappen et al. [16] showed that the semiconductor Bloch equations predict different emission spectra for different polarization configurations only if the equations include corrections to the standard approximations. A theoretical treatment of the coherent response of \( E_0 + \Delta_0 \) excitons with a multiple-band model (including the split-off band) for the semiconductor Bloch equations has not been presented in the literature. It is possible that the contributions to the coherent response from the correction terms may explain the observations reported here. This possibility has not been investigated as part of this thesis and remains an open issue.

An explanation of the SR-FWM results based on interference between an EID \( E_0 + \)
\( \Delta_0 \) exciton contribution and a continuum photon echo contribution was considered as an alternative to the Fano interference model. Screening of the hole-phonon interaction could produce \( E_0 + \Delta_0 \) exciton emission out of phase with the photon echo emission. However, the screened hole-phonon model inaccurately predicts the density scaling behaviour of the width of the emission peak at \( E_0 + \Delta_0 \). In addition, at the lowest density only the \( E_0 + \Delta_0 \) exciton contribution was spectrally resolved and therefore the SR-FWM spectrum cannot be the result of interference between two polarizations, since the photon echo was very weak. Therefore the EID mechanism was ruled out as a possible explanation of the SR-FWM results near \( E_0 + \Delta_0 \).

This thesis is the first investigation of coherent electron dynamics near the \( E_0 + \Delta_0 \) transition in a III-V semiconductor. InP was studied instead of GaAs because the \( E_0 + \Delta_0 \) transition energy of InP is well below the threshold energy for intervalley scattering in the conduction band, whereas these two energies are comparable in GaAs. To focus on the \( E_0 + \Delta_0 \) transition and to avoid effects related to intervalley scattering, InP was chosen for this work. An investigation of the coherent response near \( E_0 + \Delta_0 \) in GaAs and InGaAsP alloys would be very interesting. The first observation of coherent emission associated with the \( E_0 + \Delta_0 \) exciton has been presented and provides new insight into the decay mechanisms and interactions of \( E_0 + \Delta_0 \) excitons.
Appendix A

Laser Alignment

A method for aligning the Ti:sapphire laser for mode-locked (ML) operation is presented here. A description of the laser is contained in section 3.1. References are made to optics as labeled in Fig. 3.1. A detector with at least 100 MHz bandwidth is required to observe the ML state. The ability to inspect the spatial mode will be useful to ensure reasonable mode quality is achieved, although the alignment procedure given here does not include any information about the spatial mode.

The first step is to obtain stable continuous wave (CW) operation. The mirror M1 is made of quartz and is birefringent; it must be rotated so that the pump beam polarization is not rotated (i.e. polarization aligned along either the fast or slow axis). Typically, the threshold should be 1 W and the output slope efficiency should be 20–25 %. The spatial mode should be round and free of any distortions. The tuning slit should not be clipping the beam. The output power should not be very sensitive to small displacements of the rod or mirror M2 along the cavity axis. The separation between the prisms is a critical distance. The laser will mode lock much more easily with negative total cavity dispersion. Starting with a prism separation of 50 cm for LaKL21 glass prisms will facilitate obtaining ML operation.

Typically, two adjustments are made to obtain an alignment suitable for ML operation. First, move the curved mirror M2 away from the rod by about 200 microns, while gently pushing on the translation stage of prism P1 your thumb. The output power should not decrease by more than 20 % as the mirror is moved. While continuously pushing on prism P1, make fine adjustments of the axial position for both the rod and M2. The laser output should be very noisy on a 100 MHz timescale, when it is close to mode locking. If not, move M2 further away from the rod. At some point, the laser will mode lock and fine adjustments can be made of the axial positions. The range over which the laser will mode
Appendix A. Laser Alignment

lock for either the rod or M2 axial position is typically 5–10 microns. Commonly, the amount of insertion of the prisms must be fine tuned.

An alternate procedure that has worked well at times is to initially move M2 toward the rod by about 100 microns. Typically the rod position will need to be moved more than in the above procedure. For a complete alignment procedure consult the booklet *Mode-Locked Ti:Sapphire Laser*[77].

Some typical problems and difficulties that arise are the following. Self Q-switching appears as a mode-locked train of pulses under a modulation envelope of approximately 300 kHz and almost 100% depth. It occurs if the adjustments from the starting point are too drastic. It can be avoided by improving the CW operation initially. The ML train can have more than one pulse per round trip time. Typically the laser double pulses but can triple or quadruple pulse as well. This problem can be difficult to identify because the time between pulses can be anywhere from 1 ps to 6 ns. A separation below 10 ps would show up in an autocorrelation trace and a separation above 1 ns would be detectable on an oscilloscope. The laser can double pulse with a separation in the 10–100 ps range. It occurs because the intracavity peak intensity is too high. To reduce the peak intensity, the pump power can be reduced or the pulse width broadened by increasing the amount of glass in the cavity with one prism. The optimum intensity level is dependent on alignment. Improving the initial CW operation may alleviate the problem too. The laser can mode lock in almost any spatial mode imaginable. For best ML modes, minimize the deviation from best CW operation. By sacrificing a little power in the initial CW mode, the deviation to ML mode can be reduced. Move M2 toward the rod and optimize the CW cavity in a few iterations. The output power may drop somewhat (10%) but the ML mode may be better.

Although the procedure may appear poorly defined, with a little experience one learns to identify the signatures of the mode locking behaviour. The best advice I was given while building the laser was, “It will work.”
Appendix B

Electronic Circuits

For spectrally integrated measurements, a subtractor circuit was used to reduce laser noise. Typically 10 dB voltage noise reduction was achieved. The circuit was originally built for time-resolved transmission measurements[94] but was modified by me for these FWM measurements. The primary modifications were to remove the cascode and matched transistor pair. The circuit is shown in Fig. B.1. This circuit also provides the attractive feature that the output can be effectively AC coupled without a low-pass filter thus avoiding signal distortion.

![Subtractor circuit diagram](image)

Figure B.1: Subtractor circuit used to reduce laser noise in spectrally integrated FWM measurements.

For spectrally resolved measurements, an AC-coupled impedance reducer was used to avoid bandwidth limitation posed by the cable capacitance. Since the photomultiplier is negatively biased a p-type FET was used. The circuit is shown in Fig. B.2. The same
bandwidth limitation problems were faced for the autocorrelation measurements. A similar circuit but with an n-type FET was used for autocorrelation measurements.

Figure B.2: Impedance matching circuit for a photomultiplier.
References


[80] M. Piché, private communication.


