RESONANCE RAMAN SCATTERING IN SEMICONDUCTORS

by

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PREFACE

Light scattering has received a tremendous impetus in recent years due to the advances in low-power gas lasers. This phenomenon has become a powerful means of probing the basic properties of matter and has stimulated the industrial development of a variety of lasers such as He-Ne, ionized Ar, Kr. Basically, light scattering can be used as a probe to study the electronic structure and electron-phonon interaction in semiconductors. This study is particularly fruitful when the frequency of the exciting radiation is near one of the allowed optical transition frequencies of the medium. This is because there is an enhancement in the Raman scattering cross-section under this condition. This enhancement of Raman scattering cross-section for the laser energy near a critical point energy is called resonant Raman scattering.

Resonant Raman scattering in semiconductors has been studied at length both theoretically and experimentally[1]. The first theoretical description of resonance Raman scattering in semiconductors was given by Loudon[2] who considered free electron-hole pairs as intermediate scattering states. A comparison of this theory with the results of early experiments[3,4] on resonance Raman scattering in semiconductors at M_0 critical point showed that the observed enhancements in cross-section were incompatible with the predictions of Loudon's theory. A more complete theory was later given by Ganguly and Birman[5,6] for hydrogenic excitons as intermediate scattering states. Their theory was found to give correct results at the M_0 edge, but it failed at the saddle-points. This is because at a saddle-point an exciton is no longer hydrogenic. Other theories[7-10] have also been proposed for resonance Raman scattering in semiconductors, but none of these theories could account for the observed behaviour of Raman scattering cross section at the M_1 saddle-point. Therefore, it is meaningful to formulate a theory of resonance Raman scattering at saddle-points of semiconductors, which would explain, at least qualitatively, the observed features.

The present thesis is divided into two parts. In the first part a theoretical formulation of one-phonon resonant Raman scattering at the critical points of semiconductors is given and the theory is applied to zincblende crystals. Emphasis is placed on scattering near the saddle-points. The Raman scattering amplitude has been calculated in the vicinity of various critical points for both interacting and non-interacting electrons.

The calculations have been made under the assumption that the scattering matrix elements are momentum independent i.e. the dominant electron-phonon coupling is of the deformation potential type.

The second part of the thesis deals with a theoretical treatment of resonance Raman scattering near the excitons in Cu_2O. Resonance Raman scattering in Cu_2O has been studied at great length experimentally. This is due primarily to the fact that its optical properties have been studied extensively in the past and because its exciton energies fall within the range of available laser energies. The refined experiments have led to the observation of resonance effects at 1s yellow exciton, whose excitation is dipole-forbidden. Multiple resonance effects have also been observed at the n=2 and higher excitons of the yellow series.

The entire work will be presented in six chapters. The important points concerning each chapter are given below.

In the first chapter, the formulation of a general theory of one-phonon resonant Raman scattering of light at the critical points in semiconductors is discussed in great detail. As mentioned before, both interacting and non-interacting electrons are considered as intermediate scattering states in the formulation of the theory. The effect of electron-hole interaction is discussed within the framework of the Slater-Koster model. The Coulomb nature of electron-hole interaction at saddle-points and its effect on Raman scattering is also discussed. In both cases enhancement in scattering is predicted near the saddle-points, in addition to resonant scattering near the metastable exciton energies.

The work done in this chapter has resulted in the following publication:

> "Resonant Raman Scattering at the Critical Points of Semiconductors" - Physical Review B, Vol.8, 676, 1973.

In chapter two the theory, in a slightly modified form, is applied to zincblende crystals. The one-phonon Stokes-Raman cross-sections are computed numerically for InAs, GaAs and InSb using an empirically determined joint density of states. These calculations clearly indicate a correlation between the structure in the energy-dependent Raman cross-sections and the Van Hove critical points. The broad essential features of light scattering near the M_1 edge are brought out by the results. These are large resonance enhancements, deep minima between the resonances and large absolute cross-sections. Finally, the theory is compared with the available experimental data on InAs, GaAs and InSb[11-15].

The results of this chapter have appeared in the following papers:

"Resonance Raman Scattering at the Saddle-Points of Semiconductors" - Physics Letters 42A, 215, 1972.

"Resonance Raman Scattering at the Critical Points of Zincblende Crystals" - Physica Status Solidi B, Vol.60, 855, 1973.

Chapter three discusses in detail the dipole scattering at the forbidden yellow exciton in Cu_2O. The 1s yellow exciton in Cu_2O being dipole-forbidden, dipole scattering at this exciton occurs via a two-phonon process. Two-phonon dipole resonance Raman scattering near the forbidden yellow exciton in Cu_2O has been observed experimentally by Falicov et al[16]. In this chapter the theory of two-phonon Raman scattering at a forbidden exciton is worked out and the two-phonon amplitudes calculated on the basis of this theory. The theory is then compared with the experimental results.

Strong resonant enhancement of the first-order

Raman lines of the normally forbidden odd-parity phonons has been recently observed by Compaan and Cummins[17] in Cu_2O at the dipole-forbidden 1s yellow exciton. The appearance of these odd-parity phonons in the scattering is explained by the fact that the exciton-radiation interaction near the 1s yellow exciton is of electric quadrupole nature. The resonance enhancement of these Raman lines is explained by including the electric quadrupole term of the exciton-photon interaction in the calculation of Raman cross-section. In the fourth chapter the theory for one-phonon dipole resonance Raman scattering has been modified to include the electric quadrupole term of the exciton radiation interaction and the Raman cross-sections have been calculated. Again, the theory is compared with the experimental data.

The fifth chapter discusses resonance effects at n=2,3,4, ... excitons in Raman scattering in Cu_2O. Sharp resonance enhancements have been observed by Yu and Shen[18] in some two-phonon Raman modes of Cu_2O around the n=2 to n=6 peaks of the yellow exciton series. On the high-energy side of each resonance there is an antiresonance. A similar situation arises in the case of absorption spectra where again one finds antiresonances on the high-energy side of the peaks.

Antiresonances in the absorption spectra are caused by interference of the exciton with the continuum due to the background of one-electron absorption. Similar interference effects show up in the experiments of Yu and Shen[18]. In this chapter, a theory incorporating the interference effects is formulated and is compared with the experimental results.

In the sixth chapter we have summarized and discussed the main results of the thesis and have outlined the scope for further work.

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