PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 559–562

HYPER-RAMAN SCATTERING IN CdS AND ZnO IN STRONG MAGNETIC FIELDS

G.Kurtze and W.Maier
Hochfeldmagnetlabor der Max-Planck Gesellschaft, F 38042 Grenoble, France
K.Kempf, G.Schmieder, H.Schrey and C.Klingshirn
Institut für Angewandte Physik der Universität, D 7500 Karlsruhe, FRG
B.Hönerlage and U.Rössler
Institut für Theoretische Physik der Universität, D 8400 Regensburg, FRG

Using two-photon- (or hyper-) Raman scattering (HRS), the dispersion curves of excitons (x) and excitonic polaritons are investigated in CdS and ZnO. For the theoretical description the Hamiltonian describing the 8-fold exciton ground state is constructed from an invariant expansion. First we give the dispersion curves without external perturbation, then we present the influence of a magnetic field. Finally we discuss renormalization effects introduced by the presence of excitons or polaritons at high density.

I. Theoretical Description of Excitons and Excitonic Polaritons

The upper three valence bands in wurtzite II-VI compounds are called A, B, and C. Since the splitting ΔAB of the A- and B-valence band is small compared to ΔBC we take only the A and B bands into consideration. They have the symmetries $A\Gamma_9 (A\Gamma_7)$ and $B\Gamma_7$ $(B\Gamma_9)$ for CdS (ZnO). Together with the Γ_7 conduction band we get 8 almost degenerate x-states with symmetries $2A\Gamma_6$, $2A\Gamma_5$, $B\Gamma_1$, $B\Gamma_2$, $2B\Gamma_5$ $(A\Gamma_1, A\Gamma_2, 2A\Gamma_5, 2B\Gamma_6, 2B\Gamma_5)$ for CdS (ZnO). We construct the corresponding perturbation matrix from an invariant expansion, using the quasicubic approximation [1]. For $\underline{k} = 0$ there appear in the main-diagonal (MD) the x-energies modified by the crystal field, the spin-orbit coupling and the exchange interactions. Additionally there are some off-diagonal (OD) elements brought about by the quasi-cubic approximation. For $\underline{k} \neq 0$ effective mass terms appear in the MD. $\underline{k}$-linear OD-terms are possible for all Γ_7 bands. We neglect here those connected with the conduction band and consider only those for the Γ_7 valence band. $\underline{k}$ and $\underline{k}^2$ induced exchange terms and warping terms are neglected.

A magnetic field $\underline{B}$ introduces MD terms αB^2 describing the diamagnetic shift and OD-terms linear in $\underline{B}$ (Zeemann effect) with the corresponding g-factors. $\underline{B}\cdot\underline{k}$ mixed terms are assumed to be small and are neglected. For CdS it is sufficient to use the A-x since Δ_{AB} is large compared to the splitting of the A-x; for ZnO we use the full 8-fold x-space.

The matrices are diagonalized yielding the eigenenergies $E(\underline{k})$ and the corresponding eigenvectors. The x are coupled to the radiation field using eq. (3) in [2], modified for uniaxial crystals. These rather complex dispersion curves are introduced in a computer program which allows us to describe the HRS process for different scattering geometries. The HRS program in turn can be extended e.g. by adding additional resonances which may appear at high excitation density I_{exc} (see IIc).

II. Experimental Results and their Comparison to Theory

The experimental setups correspond to those described e.g. in [3,4]. In the conversion of wavelength to photon energies we use the appropriate refractive index of air n_a. This reduces all energies by about 0.7 meV and 1 meV for CdS and ZnO, respectively, as compared to values where n_a is assumed to be exactly one.

a. Results without magnetic field

The HRS measurements for CdS are consistent with dispersion curves calculated with the following parameters: $E_{\Gamma_5^T} = 2.5521$ eV; $\Delta_{LT} = 2.2$ meV; $\Delta_{\Gamma_5^T\Gamma_6} = 0.2$ meV [5]; $\varepsilon_b \approx 8.0$; $m_{x\perp c} = 0.9\ m_o$; $m_{x\parallel c} = 3.0\ m_o$. The comparison between experiment and theory is given in Fig. (1a). In [3] a similar analysis led to a somewhat higher value of Δ_{LT} and to a suprisingly low value of ε_b, which was attributed to high-excitation effects. We now understand these effects in some more detail (see IIc) and we are able to fit the experimental HRS data with conventional data for ε_b and Δ_{LT}, which agree with those deduced e.g. from reflection and Brillouin scattering (see e.g. [3,5,6] and the literature cited therein). The results for ZnO are shown in Fig. (2a) now using the 8-fold x-space and <u>k</u>-linear terms in the A-x. The parameters are $E_{A\Gamma_5^T} = 3.3755$ eV; $\Delta_{ALT} = 1.5$ meV; $\Delta_{A\Gamma_5^T\Gamma_2} = 0.2$ meV; $\Delta_{A\Gamma_1\Gamma_2} \approx 0$; $E_{B\Gamma_5^T} = 3.3811$ eV; $\Delta_{BLT} = 11.2$ meV [6]; $\Delta_{B\Gamma_5^T\Gamma_6} \approx 0.35$ meV; $m_{\parallel,\perp,A,B} = 0.87 m_o$ [6]; $\varepsilon_b = 6.2$; $c = 2\cdot10^{-10}$ eV cm [6]. Our absorption measurements agree with the luminescence results in [6].

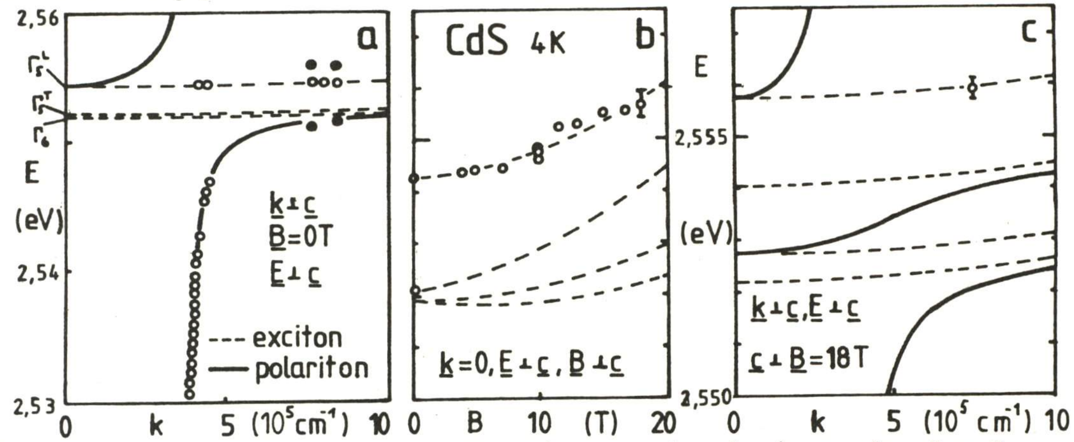

Fig.(1) The dispersion curves of excitons and polaritons for <u>B</u> = 0 (•) from [3] (a), the shift of the exciton energies with <u>B</u> (experimental points extrapolated to <u>k</u>=0) (b), and the dispersion curve for B=18T (c)

b. Results with Magnetic Field

Figure (1b) and (2b) give the shifts and splittings of the x-eigenenergies in magnetic fields up to 20 T for CdS and ZnO, respectively, together with experimental results from HRS and absorption.

In CdS, the g-values are well-known ($g_e = 1.75$ isotropic, $g_{h\Gamma_9} = 2.76 \cos\measuredangle(\underline{B},\underline{c})$ [4,7]). So we are able to deduce the diamagnetic shifts: $\alpha_{B\perp c} = 3.5\cdot10^{-6}$ eV/T^2; $\alpha_{B\parallel c} = 4.8\cdot10^{-6}$ eV/T^2. These values are slightly higher than values calculated from the x-radius, but they show the correct anisotropy. Figure (1b) is consistent with calulations in [8]. For ZnO, the g-values are not very presicely known [6]. We assume $g_e=2.1$ (isotropic), $g_{h\Gamma_7\parallel c}= 1.7$; $g_{h\Gamma_7\perp c}\approx 1.2$; $g_{h\Gamma_9}=2 \cos\measuredangle(\underline{B},\underline{c})$.

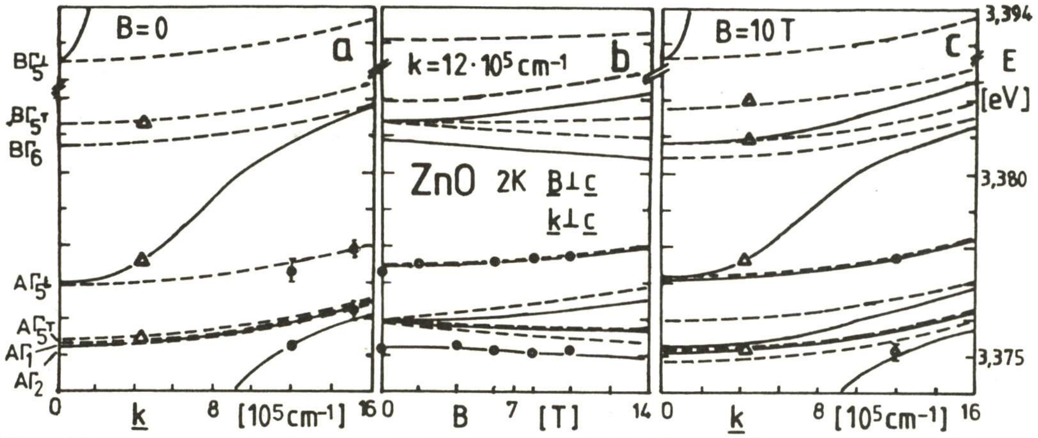

Fig.(2) The same as Fig.(1) but now for ZnO including the B-excitons and giving in (b) the eigenenergies for $k = 12 \cdot 10^5 \mathrm{cm}^{-1}$ (o $\hat{=}$ HRS, Δ $\hat{=}$ absorption $\underline{E} \parallel \underline{c}$)

The diamagnetic shift is much smaller in ZnO; $\alpha \lesssim 10^{-6} \mathrm{eV/T}^2$. In Fig. (1c) and (2c), we present the dispersion curves for CdS and ZnO at 18T and 10 T, respectively.

We limit ourselves here to $\underline{k} \perp \underline{c}$ and $\underline{B} \perp \underline{c}$. Results for other scattering geometries are given elsewhere.

c. Renormalization Effects at high Excitation Intensities

To clear the problem of ε_b in [3], we measured HRS in forward scattering under small angles. This configuration is most sensitive on ε_b. The accuracy of the angles was better than 1°. The experimental points(Fig.(3a)) cannot be fitted with normal HRS ($\Delta\varepsilon_b = 0$). It is well known, however, that the refractive index is a function of I_{exc}. We introduced such a dependence in the HRS program, by variing ε_b for the incident beam. For the Raman photons we used the unchanged dispersion curves of Fig.(1a). The calculations for negative and positive values of $\Delta\varepsilon_b$ are shown in Fig.(3a). With $\Delta\varepsilon/\varepsilon \approx 4 \cdot 10^{-3}$ we are able to fit the experiments here and with somewhat higher values in [3]. $\Delta\varepsilon/\varepsilon = 4 \cdot 10^{-3}$ corresponds to $\Delta n/n = 2 \cdot 10^{-3}$. This value is much higher than deduced e.g. from self-focussing experiments [9], because here all intermediate states are almost resonantly excited.

Another renormalization effect occurs at $\hbar\omega_{an}$ if a semiconductor is strongly illuminated at $\hbar\omega_{exc}$ due to strong one-photon excitation at $\hbar\omega_{an} = E_{biex} - \hbar\omega_{exc}$. This effect has been observed for forward scattering in CuCl [10] and for backward scattering in CdS [4]. Theoretical investigations are given e.g. in [11,12]. Figure (3b) shows the experimental results for CdS from [4], together with a calculated curve. The curve in Fig.(3b) is calculated without damping and with $E_{biex} = 5.098$ eV which corresponds to the value deduced by LATS [13].

The first two renormalization processes discussed here can be understood in perturbation theory as virtual and real two-photon excitation of biexcitons, respectively. Since we have always a strongly stimulated R_L-line in our experiments, a two-step excitation of biexcitons via really excited longitudinal x is possible. The anomaly should appear if either a Raman-photon or the exciting laser fulfills the condition $\hbar\omega_{R/exc} + E_L = E_{biex}$.

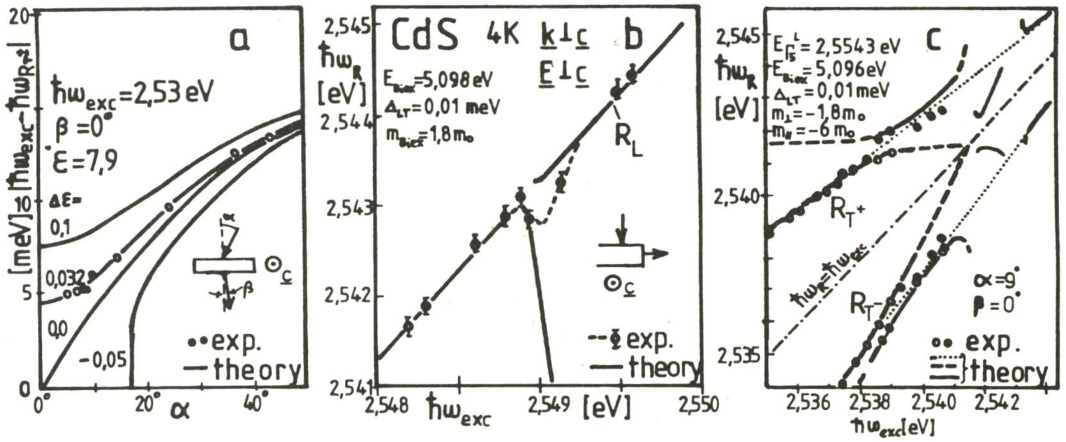

Fig. (3) Various renormalization processes which manifest themselves in the relations between $|\hbar\omega_{exc} - \hbar\omega_{R_{T+/-}}|$ as a function of the scattering angle α (a), between $\hbar\omega_{exc}$ and $\hbar\omega_{R_L}$ (b), and $\hbar\omega_{exc}$ and $\hbar\omega_{R_{T+/-}}$ (c): The masses and Δ_{LT} in (b) and (c) refer to the additional resonance used in the calculation

In the experiments we observe an anomaly for $\hbar\omega_{R_{T+}} \approx 2.5416$ eV in forward scattering. It occurs at the same spectral position for scattering angles α between 8° and 23°. We interpret this anomaly as being due to the above mentioned transition. Figure (3c) gives the calculated relation between $\hbar\omega_{R_{T+/-}}$ and $\hbar\omega_{exc}$ together with experimental points. The agreement between experiment and theory is good. Since R_{T+} and R_{T-} are correlated by energy and momentum conservation, an anomaly for R_{T+} results simultaneously in an anomaly for R_{T-}. An open problem here is the absolute spectral position of the anomaly. $E_L + \hbar\omega_{R_{T+}} = 5.096$ eV which is roughly 2 meV below the value given above. Possible explanations would be a finite kinetic energy of the longitudinal x, a transition from the upper polarition branch (not from longitudinal x) or a shift of the biexciton level as a function of I_{exc}.

1) K.Cho: Phys.Rev. B14 (1976) 4463.
2) A.Bivas, Vu Duy Phach, B.Hönerlage, U.Rössler and J.B.Grun: Phys.Rev. B20 (1979) 3442.
3) H.Schrey, V.G.Lyssenko, C.Klingshirn and B.Hönerlage: Phys.Rev. B20 (1979) 5267.
4) G.Kurtze, W.Maier, G.Blattner and C.Klingshirn: Z.Physik, B39 (1980) 95.
5) I.Broser and M.Rosenzweig: Verhandl.DPG (VI)15 HL 258 (1980).
6) K.Hümmer, R.Helbig and M.Baumgärtner: phys.stat.sol. b86 (1978) 527, and K.Hümmer. Habilitation-thesis, Erlangen (1978).
7) D.G.Thomas and J.J.Hopfield: Phys.Rev. 175 (1968) 1021.
8) J.Röseler and K.Henneberger: phys.stat.sol. b93 (1979) 213.
9) A.A.Borshch, M.S.Brodin and N.N.Krupa: JETP 43 (1976) 940.
10) T.Itoh and T.Suzuki: J.Phys.Soc.Jap. 45 (1978) 1939.
11) V.May, K.Henneberger and F.Henneberger: phys.stat.sol. b94 (1979) 611.
12) H.Haug, R.März and S.Schmitt-Rink: Physics Letters, 77A (1980) 287.
13) H.Schrey, V.G.Lyssenko and C.Klingshirn: Sol.Stat.Com. 32 (1979) 897.