Symmetry Assignment of the Direct Band Gap of TlCl and Evidence for Exciton Intervalley Scattering by Stress Optical Experiments*

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The doublet structure observed for the first exciton transition in TlCl is investigated with the aid of uniaxial stress. It is shown experimentally that the direct energy gap belongs to point $X=(\pi/a)(001)$ of the Brillouin zone. The exciton structure following from this identification is discussed, and a new interpretation of the doublet splitting based on X-point degeneracy is suggested. First conclusive evidence is given for intervalley scattering of direct excitons created by transitions outside the center of the Brillouin zone.

According to recent band structure calculations by Overhof and Treusch[1] the fundamental energy gap of TlCl occurs at point X of the cubic Brillouin zone. With spin-orbit coupling, the upper valence band and the lowest conduction band at X are both twofold degenerate and of symmetry X_6^+ and X_6^-, respectively. The presence of three inequivalent X points in the Brillouin zone causes some interesting questions concerning the exciton structure. In contrast to comparable Γ-point transitions, the higher degeneracy of X excitons may cause fine structure when lifted by some kind of interaction, e.g., intervalley scattering of particles between different X points.

In this Letter the assignment of the energy gap of TlCl to point X is confirmed experimentally by stress optical experiments. On the basis of this identification we can explain the doublet structure[2] of the first exciton band as being caused by an intrinsic mechanism and not by residual strain splitting. The stress behavior of this band also gives evidence for intervalley scattering, which is revealed by interference with the stress induced interactions.

The experiments were carried out on single crystals of TlCl. After annealing at 200°C high-quality sample surfaces were obtained by etching in hot water. A static uniaxial pressure was applied to the sample within the elastic deformation range, and reflectivity spectra were recorded with light polarized either parallel or perpendicular to the stress direction. In well-prepared samples the zero-stress spectrum did not depend on polarization direction and on the specific sample orientation. In particular the zero-stress splitting was found to be the same in all these samples. We take this as an indication that no internal strains were present. Kramers-Kronig analysis was performed using additional vacuum-uv data[3] and refractive-index[4] data in order to calculate the imaginary part ϵ_2 of the dielectric function.

Figure 1 shows the calculated ϵ_2 spectra in the region of the first exciton for different amounts of pressure applied in the (001) direction. The zero-stress doublet structure A, B changes to a five-component structure in the strained crystal. Three components are visible for perpendicular and two for parallel polarization. With increasing pressure a drastic exchange of oscillator

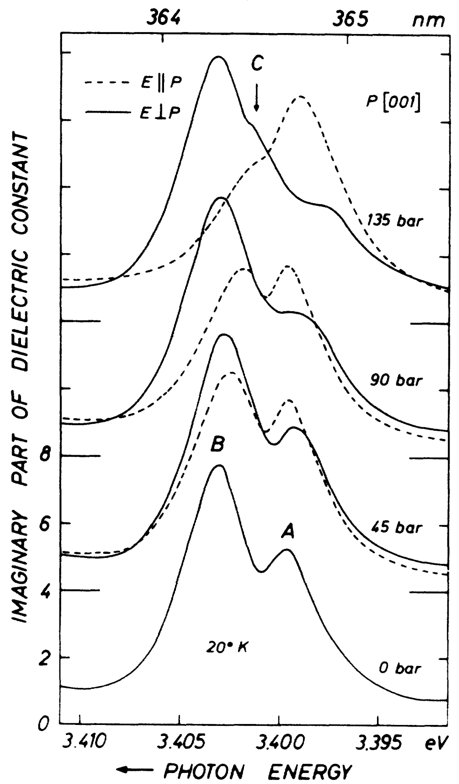

FIG. 1. Imaginary part of the dielectric constant of uniaxially stressed TlCl in the exciton region calculated from reflectivity data. Note shift of ordinate scale for different pressures.

strength occurs. For parallel polarization oscillator strength is transferred from the high-energy peak B to the low-energy peak A, and both peaks are shifted to lower energies. For perpendicular polarization the high-energy peak B remains almost unchanged, whereas the lower peak A decreases in favor of a third band C which shows up between A and B. If the pressure is applied in the (111) direction, no changes can be seen in the spectrum apart from an overall hydrostatic shift to lower energy. This behavior immediately allows the conclusion that the direct energy gap of TlCl is not situated at point Γ or R as formerly assumed.[5,2] On the other hand, the pressure results confirm the prediction of the band calculations[1] that the direct gap occurs at X.

In the following we try a phenomenological analysis of the observed spectrum under the assumption that the exciton states are constructed from X_6^+ holes and X_6^- electrons via a $1s$-type envelope function. Taking the band and star degeneracy into account there are 36 possibilities to form $1s$ excitons from these states. Because of the optical selection rules we need only regard excitons with vanishing translational momentum, with a nonvanishing singlet spin component, and transforming according to a vector representation. There remain nine exciton states $\Psi_\mu{}^\nu$, where $\mu = 1, 2, 3$ denotes the number of the X point at which the direct transition takes place and $\nu = x, y, z$ characterizes the polarization of the transition dipole moment of the exciton.[6] In order to construct symmetry-adapted basis functions from these states we have to reduce the representation induced by the functions $\Psi_\mu{}^\nu$ under the operations of the point group O_h of TlCl. We find the linear combinations

$$\Phi_{\rm I}{}^x = \tfrac{1}{2}\sqrt{2}(\Psi_2{}^x + \Psi_3{}^x), \quad \Phi_{\rm II}{}^{yz} = \tfrac{1}{2}\sqrt{2}(\Psi_2{}^x - \Psi_3{}^x), \quad \Phi_{\rm III}{}^x = \Psi_1{}^x, \tag{1}$$

and six other combinations which can be derived by simultaneous cyclic permutation of μ and ν.

The sets $\Phi_{\rm I}$ and $\Phi_{\rm III}$ transform according to Γ_4^-, the set $\Phi_{\rm II}$ according to Γ_5^- under the operations of the cubic point group. Only excitons of type I and III are dipole active; therefore it is obvious to attribute these levels to the two components A, B of the first TlCl exciton transition which is visible in the spectrum.[2] The combination of type II cannot be seen because the transition dipole moments cancel.

The details of the spectrum and its pressure dependence can be understood by setting up a formal Hamiltonian matrix for the states $\Phi_{\rm I}$, $\Phi_{\rm II}$, and $\Phi_{\rm III}$ including the (001) pressure perturbation. The matrix elements for parallel polarization (z-type excitons) and perpendicular polarization (e.g., x-type excitons) are given in Table I. There appear three diagonal matrix elements E_1, E_2, and E_3 and one nondiagonal matrix element $M_{\rm iv}$ of the unperturbed Hamiltonian. The diagonal matrix elements contain intravalley and intervalley contributions, where $M_{\rm iv}$ contains only intervalley scattering. This can be seen by inspection of formula (1). Further, Δ_1 represents the hydrostatic deformation energy shift of the gap, and $\frac{3}{2}\Delta_3$ corresponds to the tetragonal shear splitting of the star of X.[7] As can be seen from Fig. 1, the qualitative predictions of this exciton Hamiltonian concerning the pressure dependence of the spectrum are fulfilled: For parallel polarization only two peaks will be seen, whereas for perpendicular polarization the state $\Phi_{\rm II}$ is coupled to the dipole-active state $\Phi_{\rm I}$ via the matrix element $-\frac{3}{4}\Delta_3$ and therefore becomes visible as band C between bands A and B.[8]

The doublet structure A, B does not vanish for zero stress because E_1 and E_3 may be different and the coupling matrix element $M_{\rm iv}$ further splits the states. The pressure-induced exchange of oscillator strength between the components A and B for parallel polarization is only possible if the matrix element $M_{\rm iv}$ does not vanish. As pointed out this matrix element describes an interaction of direct excitons centered on different X points of the Brillouin zone. In contrast to the

TABLE I. Matrix elements of the exciton Hamiltonian including the effect of (001) stress.

	$\Phi_{\rm I}{}^z$	$\Phi_{\rm II}{}^{xy}$	$\Phi_{\rm III}{}^z$		$\Phi_{\rm I}{}^x$	$\Phi_{\rm II}{}^{yz}$	$\Phi_{\rm III}{}^x$
$\Phi_{\rm I}{}^z$	$E_1 + \Delta_1 - \frac{\Delta_3}{2}$	0	$M_{\rm iv}$	$\Phi_{\rm I}{}^x$	$E_1 + \Delta_1 + \frac{\Delta_3}{4}$	$-\frac{3}{4}\Delta_3$	$M_{\rm iv}$
$\Phi_{\rm II}{}^{xy}$	0	$E_2 + \Delta_1 - \frac{\Delta_3}{2}$	0	$\Phi_{\rm II}{}^{yz}$	$-\frac{3}{4}\Delta_3$	$E_2 + \Delta_1 + \frac{\Delta_3}{4}$	0
$\Phi_{\rm III}{}^z$	$M_{\rm iv}$	0	$E_2 + \Delta_1 + \Delta_3$	$\Phi_{\rm III}{}^x$	$M_{\rm iv}$	0	$E_3 + \Delta_1 - \frac{\Delta_3}{2}$

case of indirect excitons[9] this interaction is not forbidden by translational symmetry. It may be realized in the form of simultaneous scattering of electrons and holes between different X points by either Coulomb or electron-phonon interaction.

A quantitative determination of the matrix elements in question and the deformation potentials is difficult because of uncertainties in the decomposition of overlapping bands A, B, and C. At the present time we can only give a rough estimate of these quantities. Using the hydrostatic deformation potential[10] to eliminate Δ_1 we find that $\Delta_3 \approx 7$ eV per unit shear deformation $\frac{2}{3}e_{zz} - \frac{1}{3}(e_{xx}+e_{yy})$. This rather large value again indicates that the exciton transition does not take place at the center of the Brillouin zone but that a star degeneracy is involved. Preliminary analysis shows that $E_1 < E_2 < E_3$ with $E_3 - E_1 \approx 3$ meV and that the scattering matrix element M_{iv} is about 1 meV. The same scattering mechanism presumably also holds for TlBr where a similar but smaller splitting of the first exciton band is observed.[2]

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[6] It is understood that X points 1,2,3 lie in k_x, k_y, k_z directions, respectively.

[7] The stress shift and splitting of the energy gap follows a relation similar to that quoted by H. Brooks, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic, New York, 1956), Vol. 7, p. 85 ff.

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Impurity-Induced Nuclear Spin-Lattice Relaxation in Metals: A New Approach

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We find an $\exp[-(t/\tau_1)^{1/2}]$ time dependence for the recovery of the Al^{27} nuclear magnetization in the system $\mathrm{La}_{1-c}\mathrm{Gd}_c\mathrm{Al}_2$. This is characteristic of diffusionless relaxation and an especially direct interpretation of the data is possible in this limit. Variation of τ_1 with temperature and magnetic field indicates that longitudinal dipolar fluctuations of the Gd moments relax the Al^{27} nuclei while its concentration dependence indicates Ruderman-Kittel-Kasuya-Yosida coupling between the Gd spins.

We have studied the Al^{27} nuclear spin-lattice relaxation in the system $\mathrm{La}_{1-c}\mathrm{Gd}_c\mathrm{Al}_2$. Conditions are such in these materials that contributions to relaxation from the Gd impurities can be interpreted in a way which does not depend on the poorly defined quantities[1] usually encountered in impurity relaxation studies: the diffusion constant, the diffusion barrier radius, and the observation barrier radius. This considerable simplification permits an unambiguous determination of the impurity relaxation process operative in metals which we will compare with other recent work.[2-4]

A number of interactions between the nuclei