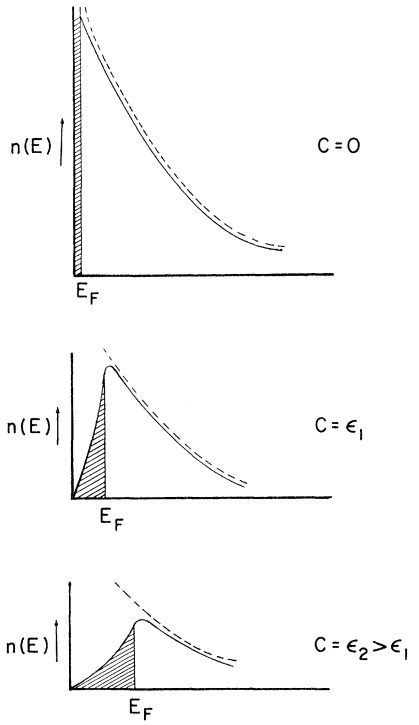

FIG. 2. Suppression of the density of states in V_3Au due to progressive degrees of disordering.

2, where a drastic suppression of $n(E)$ occurs with disordering.

In conclusion, there appears room for discussion on the mechanism for the drastic lowering of T_c with a small amount of disordering. It is still questionable whether this is directly due to a decrease in $n(E_F)$ or indirectly through the effect of $n(E_F)$ on the phonon spectrum. We suggest that further experimental data be obtained to clarify the mechanism. For example, one could measure the effects of small disorder on the phonon frequencies in V_3Au at low temperatures with neutron inelastic-scattering experiments. It would also be interesting, though less informative, to measure the effect of small disordering on the ultrasonic velocities at low temperatures.

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LUMINESCENCE FROM POLARITONS

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The intrinsic emission of CdS is studied at 20°K. We report the first clear-cut evidence of exciton polariton luminescence.

In 1958, Hopfield[1] predicted the existence of polaritons in crystals where there is strong coupling between direct excitons and photons. From absorption data Thomas and Hopfield[2-4] put into evidence a "longitudinal exciton" which can present a coupling with the electromagnetic field strongly dependent on the orientation of the wave vector of the absorbed photon. Observation of luminescence from this "longitudinal exciton" in uniaxial CdS has been reported previously[5-7] but no crucial experiments have been made to identify the origin of the observed polariton line.

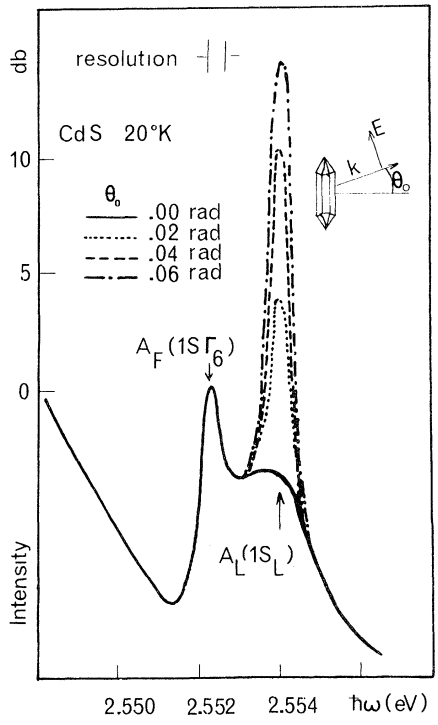

FIG. 1. Luminescence spectra for different directions of propagation. θ_0 is the angle measured outside the crystal.

We report here the first experimental study which allows one to interpret this emission in term of polaritons.

Very pure CdS platelets were excited by the 4765-Å line of an argon ion laser. Light emitted from the sample, passing through a polarizer, was focused onto the entrance slit of a Perkin-Elmer type-E_1 monochromator. In our arrangement the c axis of the crystal was horizontal. Let θ_0 be the angle between the wave vector k of the emitted photon and a horizontal vector normal to the c axis. With the help of a vertical narrow slit (1 mm width) at 10 cm from the sample we restricted θ to values located between $\theta_0 \pm \Delta\theta/2$ ($\Delta\theta = 0.01$ rad). θ_0 was varied by rotating the platelet about a vertical axis.

Typical spectra at $T = 20°K$, with various directions of propagation near $\theta_0 = 0.00$ rad, are shown in Fig. 1. The $A_F(1S\Gamma_6)$ line corresponds to the Γ_6 $n = 1$ state of exciton A.[3] This transition is theoretically forbidden at $k = 0$. The intensity of this line does not exhibit any angular dependence. The $A_L(1S_L)$ line lies approximately 2 meV above the $A_F(1S\Gamma_6)$ peak position. The positions of these lines agree fairly well with the absorption data given by Thomas and Hopfield.[3] The $A_L(1S_L)$ peak intensity increases strongly as the sample

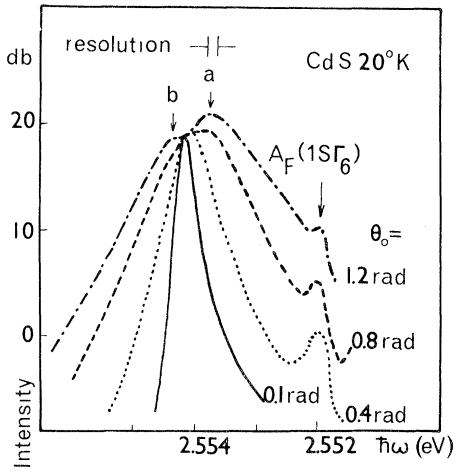

FIG. 2. Emission spectra for large values of θ_0. The different spectra have been shifted on the vertical scale by an amount such that the point ω_L is common to all curves.

is rotated about a vertical axis. For propagation exactly normal to the c axis, the line is quite unobservable and this fact seems to indicate that the transition is strictly forbidden at $\theta_0 = 0.00$ rad. We think that such behavior is due to progressive mixing of the "longitudinal exciton" with extraordinary photons inside the crystals as θ_0 is increased.

Further experiments, performed with larger values of θ_0, have shown that the $A_L(1S_L)$ line shape also depends on the direction of of propagation. These results are summarized in Fig. 2. As θ_0 is increased the line broadens on the low- and high-energy sides. The peak labeled a in Fig. 2 shifts toward lower energies. For θ_0 greater than 0.8 rad a second peak labeled b appears on the high-energy side of the line.

Our experiments are related to the A, $n = 1$ exciton energy-level structure of CdS near 2.55 eV which is shown in Fig. 3. This A exciton comes from the Γ_7 and Γ_9 conduction and valence states. The direct product $\Gamma_7 \times \Gamma_9$ transforms according to $\Gamma_5 \oplus \Gamma_6$ representations. The twofold degenerate Γ_6 exciton state is optically inactive. The electric dipole associated with the transition from Γ_5 to a fundamental state is normal to the c axis. The Coulomb interaction gives rise to a longitudinal-transverse splitting and the two Γ_5 modes of excitons are nondegenerate when the wave vector of the exciton is not parallel to the c axis. For any propagation, we have a mixed exciton (ω_m) coupled to the extraordinary photon field; the strength of the coupling is proportional to the square of its transverse component ($\sin^2\theta$).

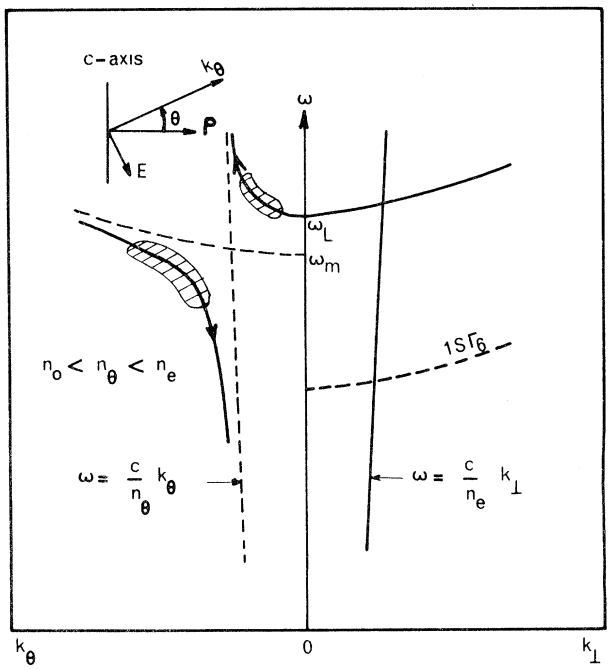

FIG. 3. On the right side are the dispersion curves for the uncoupled photons and excitons with vectors strictly perpendicular to the c axis. On the left side the dispersion curves for the modes without coupling are shown by the dashed lines; the solid lines represent the mixed modes. In the cross-hatched part of the polariton dispersion curve both exciton and photon components are of comparable size. θ is measured inside the crystal. P is the electric dipole of exciton.

There is also a purely transverse exciton which couples to ordinary waves, the coupling being constant. In our apparatus the polarizer only transmits extraordinary waves [E in the (k, c-axis) plane] and we consider in Fig. 3 only the mixed exciton with its dipole in this plane. In this way we can explain very well the data of Fig. 1.

The coupling between the mixed exciton and the extraordinary waves leads to a polariton. As θ increases from 0, the lower polariton branch shifts to lower energy while the upper branch shows a greater curvature as a result of the enhancement of the coupling. The splitting $\omega_L - \omega_m$ is given by

$$\omega_L - \omega_m = \omega_L \left(1 - \frac{\epsilon + 4\pi \cos^2\theta}{\epsilon + 4\pi\beta}\right)^{1/2},$$

where β is the oscillator strength of the line, with polarization $E \perp c$; ϵ is the high-frequency dielectric constant; and θ is the angle inside the crystal. For $\theta = 15°$ ($\theta_0 = 45°$) with $4\pi\beta/\epsilon$ from Ref. 3, we have $\omega_L - \omega_m \lesssim 0.1$ meV, while the a-b splitting observed is about 0.5 meV.

An interpretation of the luminescence data in terms of polaritons would have to follow the arguments of Hopfield.[8] A polariton of wave vector k excited at X in the crystal has a probability of reaching the surface which depends on its mean free path $\lambda(k)$. At the surface the polariton has a probability $T(k)$ of being transmitted as a (fluorescence) photon.

From the linewidth ($\Delta\omega \sim 0.3$ meV) of $A_L(1S_L)$ in the weak coupling limit (propagation almost normal to the c axis), one gets an order of magnitude of the collision time ($\tau_c \sim 0.7 \times 10^{-12}$ sec). A recombination lifetime τ_R of 10^{-8} sec was measured in an electron bombardment experiment. From these we calculated the mean free path and the diffusion length L_D for a thermal exciton (its energy is of the order of kT). At $T = 20°$K, $\lambda \simeq 300$ Å, and $L_D \simeq 1.2$ μm. Since $\lambda \ll L_D$ we see that the majority of excitonlike polaritons cannot reach the sample surface and radiate. This conclusion is reinforced by the possible existence of an inactive layer, analogous to that considered by Hopfield to explain the reflectivity data.[9] If α is the absorption coefficient of the pumping light, we have $L_D > 1/\alpha > \lambda$. In this layer the exciton density should be very small. Let us consider a dispersion curve $\omega(k)$ for θ small (Fig. 3). The polariton modes contribute differently to the fluorescence under the influence of two competing mechanisms.

(i) As we follow the polariton branches in the direction of the arrows, the collision time $\tau_c(k)$ increases while the exciton component of the polariton decreases; the group velocity $v_g(k)$ and the mean free path $\lambda(k)$ increase. Therefore photonlike polaritons can easily reach the surface. The coefficient of transmission $T(k)$ of a polariton varies from a small value when the exciton component is important to a value given by the index of refraction when the photon component is dominant. Therefore photonlike polaritons contribute the most to the luminescence.

(ii) From the line shapes of the excitons with 1 or 2 LO phonons one knows that there is in the crystal a reservoir of thermal excitons. The phase space available to these excitons is much larger than for the polaritons near the crossing point. It is reasonable to think that these polariton modes are populated by collision of excitons (from the thermal distribution of excitons) with acoustical phonons. This mechanism is a function of the exciton component of the polariton and therefore decreases as one moves away from

the crossover.

These two competing mechanisms lead to an optimum in the crossed parts of Fig. 3, which is in reasonable agreement with the a and b peaks of the data.

To this discussion we have to add the density of states. In the weak-coupling limit the two branches contribute equally, but in the strong-coupling region (θ large, $\perp$ polarization) the lower branch is much favored.

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TWO-BAND ELECTRON-PHONON INTERACTION IN RHENIUM*

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Anomalies were observed in the electronic component of the ultrasonic attenuation of transverse and longitudinal waves in high-purity rhenium, which could not satisfactorily be explained by the free-electron or real-metal theories of Pippard. A two-band model will be developed to explain the observed attenuation.

Many features of the electron-phonon interaction in metals can be explained by treating the electron system in the free-electron approximation.[1] Included is the prediction of a maximum in the ultrasonic attenuation of transverse waves for sufficiently high frequencies (about 10^9 sec^{-1}) and for $ql > 1$, where $\vec{q}$ is the impressed phonon wave vector and l is the electron mean-free path. At these frequencies the forces arising from electromagnetic coupling start to vanish and only those forces arising from collision drag remain. The maximum appears to be associated with the collision drag term and occurs for a ql value of about 2. For longitudinal waves such an effect is not predicted up to frequencies of the order of the plasma frequency (about 10^{15} sec^{-1}). Further refinements in the theory such as the inclusion of a deformation potential have led to better agreement between experiment and theory, but have not predicted additional anomalies in the ultrasonic attenuation in metals for ql on the order of 1.[2,3]

We have observed a maximum in the attenuation of transverse waves in rhenium as a function of temperature, but at frequencies an order of magnitude lower than predicted. Also, and perhaps most important, a maximum was observed in the longitudinal attenuation[4] which appeared to occur at roughly the same ql value as for the transverse waves. The two-band model to be developed below is proposed to explain this anomaly since our attempts to fit the observed attenuation to available free-electron and real-metal theories were not entirely successful.

The sample on which the measurements were taken is a rhenium single crystal 0.627 cm long by about $\frac{1}{2}$-cm diam, with a resistivity ratio in excess of 30 000. The sample ends were spark cut, polished, and etched, with crystal orientation along the [0001] axis to better than ±1°. A cadmium sulfide thin-film transducer with a shear fundamental of 200 MHz was deposited on one end.

Ultrasonic measurements were made at frequencies from 130 to 600 MHz by the pulse-echo technique, using a Matec attenuation comparator and attenuation recorder. All measurements were made for $\vec{q} \| [0001]$ direction. The estimated accuracy of the attenuation measurements is about ±2%. The temperature dependence of the attenuation coefficient was measured from 60°K to less than 0.5°K. Using a calibrated Ge resis-