the metal, and could, therefore, be expected to lower the superconducting transition temperature of group-V metals. Matthias[5] indicates that the transition temperature has maxima for electron-to-atom ratios slightly less than 5 and 7 and a minimum for e/a slightly less than 6. At hydrogen concentrations greater than VH and NbH, hydrogen seems to contribute less than one electron per atom[11] to the band structure. Thus, the superconducting transition temperature of the rather unstable hydrides VH_2 and NbH_2, which should have effective $[e/a]$ (ratio of the number of valence electrons to the number of metal atoms) values <7, may be fairly high, especially since these compounds have fcc crystal structures.[12,13]

With regard to the effect of e/a on the superconducting transition temperature, it is interesting to reflect on the aforementioned superconducting metal hydride. Th_4H_{15} would have an apparent $[e/a]>7$, but it has a high transition temperature equal to that of technetium with $e/a=7$. If this is an indication that hydrogen contributes less than one electron per atom to the band structure of thorium, then ThH_2 would have $[e/a]$ slightly less than 6 and its transition temperature would be expected to be very low.[5] Indeed, it is.[6,10]

†Work performed under the auspices of the U. S. Atomic Energy Commission.

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Exciton–LO-Phonon Interaction and the Anti-Stokes Emission Line in CdS

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Phonon interaction with the I_1 (4888-Å) emission line in CdS (exciton bound to a neutral acceptor site) has often been observed. For the first time the optical frequency anti-Stokes transition, involving the collapse of a bound exciton, has been observed in the emission from selected platelets at 1.2°K. Since the thermally excited phonon field at this temperature is negligible, the observation of anti-Stokes emission directly supports the conclusion that LO phonons are generated to a nonthermal level of distribution as the excitons decay.

Phonon sidebands on the I_1 emission line in CdS have been reported by Scott, Leite, and Damen.[1] The phonon interaction was through the $LO_{(\Gamma)}$ phonon and it was the Stokes lines that were observed. In the current experiment, emission from CdS platelet-type crystals was studied under uv excitation at low temperatures (~1.2°K). In selected crystals both the Stokes lines and an anti-Stokes line are observed. A diagram showing the general features of the emission from CdS is shown in Fig. 1. The I_1 line shows the strongest coupling to the LO phonon of any of the sharp emission lines in CdS. It is this transition that gives rise to the anti-Stokes line. The I_1 line can be removed from the crystal by appropriate heat treatment.[2] Such treatment quite naturally removes both Stokes and anti-Stokes lines.

A densitometer trace showing both the Stokes and anti-Stokes transitions is shown in Fig. 2. It has previously been shown that the Stokes transition is very sharp, in fact, so sharp that both the Γ_1 and Γ_5 LO phonons are observed. The anti-Stokes transition is somewhat broadened and this structure cannot be resolved. However, the energy of the LO phonon calculated from the anti-Stokes line is the same as the average energy

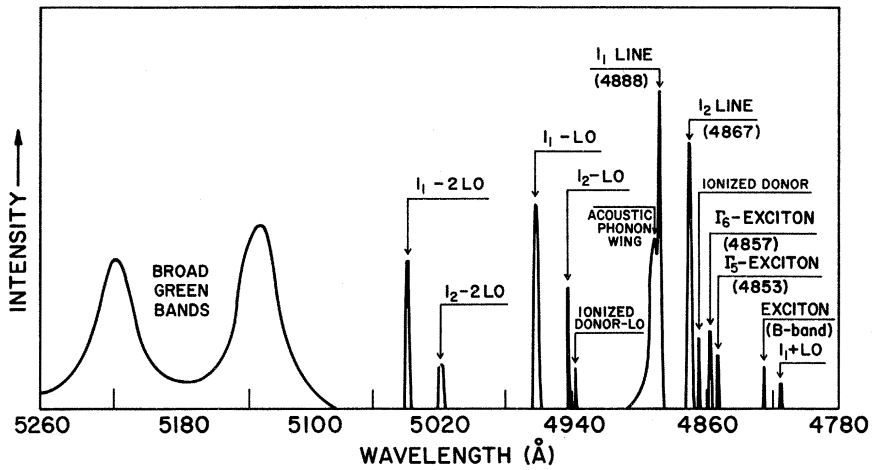

FIG. 1. Some characteristic emission lines in CdS crystals at 1.2°K.

calculated for the Γ_1 and Γ_5 phonons of the Stokes line.

A plot of the relative intensity of the anti-Stokes to that of the Stokes line as a function of exciting intensity is shown in Fig. 3. It is seen that the intensity ratio decreases as the exciting intensity decreases.

The anti-Stokes and Stokes lines correspond, respectively, to the absorption and emission of an optical phonon. The ratio of their intensities is given by

$$I_A/I_S = N_0/(N_0+1), \tag{1}$$

where N_0 is the equilibrium occupation number of the $k=0$ LO phonon. Since

$$N_0 = [\exp(\hbar\omega_0/kT)-1]^{-1}, \tag{2}$$

Eq. (1) becomes

$$I_A/I_S = \exp(-\hbar\omega_0/kT). \tag{3}$$

From Fig. 3 one can determine the intensity ratio and, substituting into Eq. (3), one can calculate the temperature required to produce the equilibrium density of phonons necessary to produce the given intensity ratio. The highest exciting intensity in Fig. 3 would require a temperature of 210°K to produce an equilibrium density of phonons sufficient to account for the measured intensity ratio of the anti-Stokes to the Stokes line. At the lowest exciting intensity a temperature of 70°K would be required to account for the observed intensity ratio. Since the experiments were performed at approximately 1.2°K one can rule out thermal generation of the phonons.

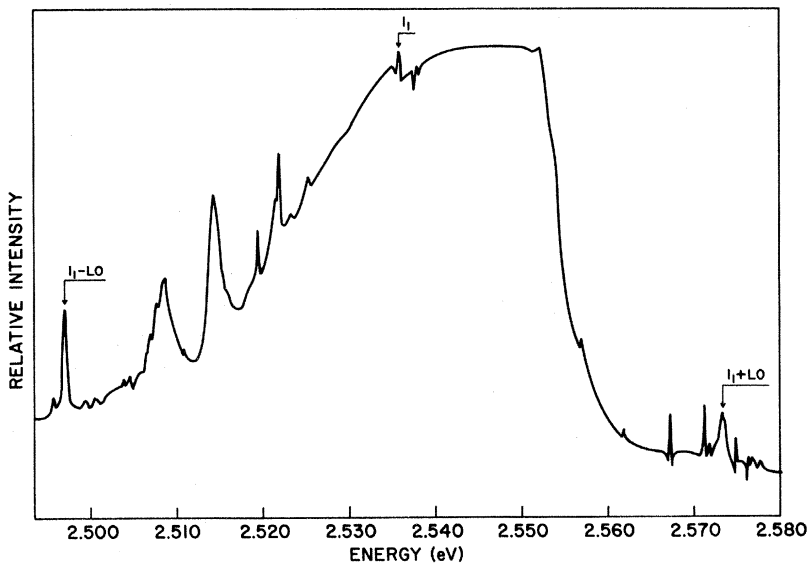

FIG. 2. A densitometer plot of the Stokes and anti-Stokes emission lines.

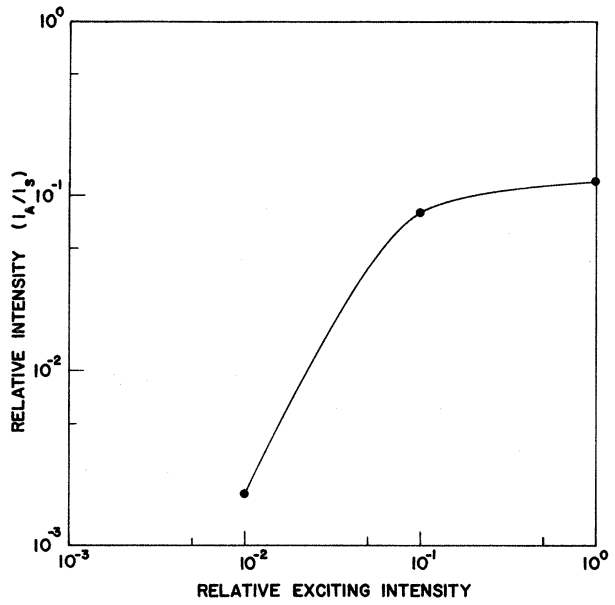

FIG. 3. A plot of the ratio of the relative intensity of the anti-Stokes to that of the Stokes transition as a function of exciting intensity.

It is well known that phonons in highly polar materials interact strongly with the LO phonon modes.

Scott, Leite, and Damen[1] have suggested that the dynamical origin of the LO-phonon sidebands in Raman effect and in luminescence are the same, and also suggest that the I_1 line in CdS is a principal intermediary. This interpretation is compatible with the giant oscillator strengths proposed by Rashba and Gurgenishvili[3] for bound excitons. The theory of "impurity" or defect absorption intensities in semiconductors has been studied by Rashba.[4] By use of the Fredholm method, he finds that, if the absorption transition occurs at $\vec{k}=0$ and if the discrete level associated with the impurity approaches the conduction band, the intensity of the absorption line increases. The explanation offered for this intensity behavior is that the optical excitation is not localized in the impurity but encompasses a number of neighboring lattice points of the host crystal. Hence, in the absorption process, light is absorbed by the entire region of the crystal consisting of the impurity and its surroundings.

In an attack on the particular problem of excitons which are weakly bound to localized "impurities," Rashba and Gurgenishvili[3] derived the following relation between the oscillator strength of the bound exciton f_d and the oscillator strength of the intrinsic excitons f_{ex}, using the effective-mass approximation:

$$f_d=(E_0/|E|)^{3/2}f_{ex}, \tag{4}$$

where $E_0=(2h^2/m)(\pi/\Omega_0)^{2/3}$, E is the binding energy of the exciton to the impurity, m is the effective mass of the intrinsic exciton, and Ω_0 is the volume of the unit cell. If the parameters for the I_1 line in CdS are substituted into Eq. (4), it is found that f_d exceeds f_{ex} by three orders of magnitude.

The efficiency of the I_1 line in generating LO phonons is determined by its oscillator strength in absorption (which creates bound excitons) and the subsequent exciton-phonon coupling when the exciton decays. The phonon generation will result from the collapse of both free and bound excitons with the emission of LO phonons. This mechanism generates an equilibrium LO-phonon field which in turn interacts with the I_1 bound exciton to give rise to the I_1 anti-Stokes emission line. This mechanism would be sensitive to the exciting intensity as is verified in Fig. 3. The fact that the anti-Stokes line comes and goes with the I_1 line, and occurs at an energy exactly a LO phonon above the I_1 lines, verifies that it is the anti-Stokes line associated with the I_1 transition.

It is also noted that in calculating the temperature effects of the intensity ratio of the anti-Stokes to the Stokes lines in Si, Hart, Aggarwal, and Lax[5] were consistently low in their calculated values in comparison with their measured values. In order to use this ratio as a temperature probe the work reported here demonstrates that one has to correct for changes in the phonon population created by the exciting radiation.

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