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Optical Absorption Edge in GaSe under Hydrostatic Pressure

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A study of the optical absorption spectrum of GaSe at the energy gap shows that the strength of the exciton line decreases as hydrostatic pressure is increased. It is proposed that this effect comes from increasing interference of the discrete exciton line with a continuum of structure due to indirect interband electronic transitions. The sign and magnitude of the pressure coefficients of the gaps in gallium chalcogenides are found to be consistent with recent band-structure studies.

Gallium selenide, GaSe, is a III-VI compound semiconductor. Its crystal structure consists of plane hexagonal lattices which are associated in pairs and may be stacked in different ways (β, γ, and ϵ modifications). Intralayer bonding is strongly covalent with some ionic contribution. Interlayer forces are mainly of the Van der Waals type.[1] Optical properties at the band edge have been studied by optical[2-8] and photoelectronic methods.[9,10] The peak in the absorption coefficient due to the ground state of the direct exciton at the band gap appears even at room temperature. An indirect gap may exist close to the direct one about 50 meV lower in energy,[11-13] but this is still under dispute.[9,14] The high-pressure behavior of gallium chalcogenides has not been directly investigated, up to now, except for a measurement of the photoconductivity edges.[9]

In this Letter, we present new data on the absorption coefficient of GaSe under hydrostatic pressure in the region of the band gap. Our results support the existence of an indirect gap close to the direct one at room pressure. The disappearance of the exciton peak with hydrostatic pressure can be explained in terms of the differential pressure coefficient of the two gaps. A qualitative explanation for the sign and magnitude of the pressure coefficients of gallium chalcogenides is proposed in the light of present band theory.

Our crystals were grown[15] by the Bridgman method and were mixtures of the ϵ and γ modifications. Samples were cleaved parallel to the layers, and normal-incidence unpolarized transmission measurements were made in a high-pressure cell with sapphire windows. Pressure was measured in the fluid (pentane) by a conventional Manganin resistance gauge.

The behavior of the absorption edge under hydrostatic pressure is exhibited in Fig. 1. The

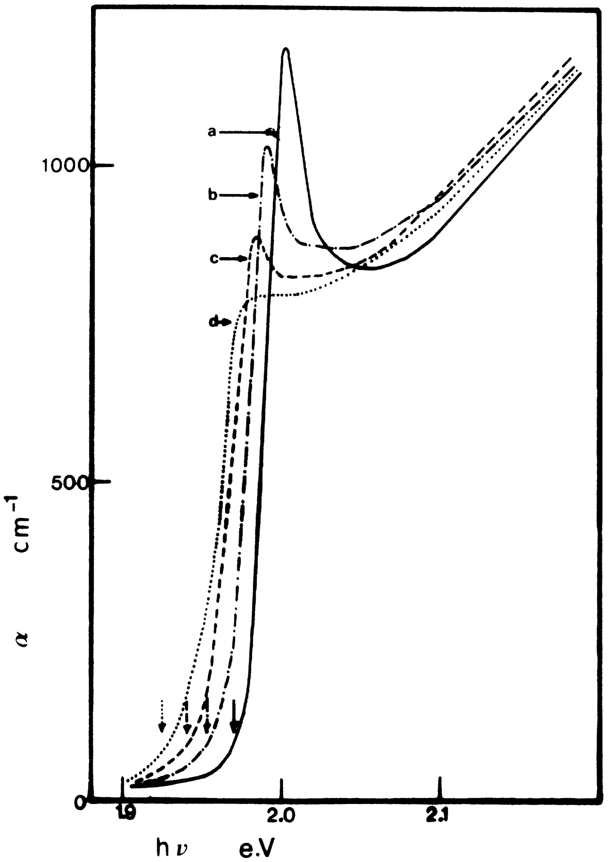

FIG. 1. Absorption coefficient for GaSe for $E \perp c$ versus incident photon energy for several pressures at 300°K. Curve *a*, full line: 1 bar; curve *b*, dash-dotted line: 2300 bars; curve *c*, dashed line: 4440 bars; curve *d*, dotted line: 6670 bars.

main features of the spectra are the following: (1) The oscillator strength of the exciton peak decreases drastically upon application of pressure. (2) The pressure coefficient of the exciton peak is $\partial E_{\text{exc}}/\partial P \simeq (-4.2 \pm 0.3) \times 10^{-6}$ eV/bar. (3) The low-energy tail for $\alpha < 200$ cm^{-1} has a pressure coefficient of $\partial E_T/\partial P \simeq (-6.5 \pm 0.6) \times 10^{-6}$ eV/bar. This low-energy edge becomes less steep when pressure is increased. (4) The absorption coefficient in the region of direct transitions (above 2.05 eV) does not change significantly.

To allow comparison of our results with those of Niilisk and Kirs,[9] under similar conditions, we indicated by arrows the maxima in their photoconductivity spectra which we interpolated from their data.

The damping of the exciton peak under pressure may be compared with the disappearance of the exciton in $\text{GaS}_x\text{Se}_{1-x}$ mixtures as x is increased.[2,12] In GaS, the exciton overlaps with a continuum associated with indirect transitions. The ratio of the strength of the continuum transition amplitude to that of the exciton increases with increasing x. Overlapping discrete and continuum states in solids have been discussed in the past,[16] using a theory due to Fano[17] to describe saddle-point excitons which are degenerate with interband continua. In this theory the interference effect between discrete and continuum states may lead to antiresonances on the high-energy side of the resonance, and a concomitant distortion of a line shape. If the interference between the two types of states is large enough, the resonance may actually disappear. This is what happens as x increases in $\text{GaS}_x\text{Se}_{1-x}$. The relative transition amplitude of the continuum and exciton states is a measure of the interference between them and it increases as x is increased.

Turning to the effect of hydrostatic pressure, it seems reasonable to expect that the pressure coefficients of the direct gap energy and that of the excitonic transition energy be about the same. The binding energy of the exciton will depend primarily upon the dielectric constant and the effective mass. These quantities will have variations with pressure of the order of the relative variation of the band gap, and should therefore introduce only second-order contributions to $\partial E_g/\partial P$ which is close to the value of -4.2×10^{-6} eV/bar. The indirect gap appears to diminish more rapidly, as indicated by the pressure coefficient of the low-energy tail which is -6.5×10^{-6} eV/bar. It should be emphasized that we do not propose this value for the indirect gap itself. This point will be discussed later.

We can now give a qualitative argument for the disappearance of the exciton peak under pressure. As the pressure is increased, the relative transition amplitude of the continuum due to indirect transitions increases with respect to that due to exciton states, because of the difference in pressure coefficients. A quantitative analysis for the effect of pressure on the exciton would require separation of the absorption spectrum into its constituent components, i.e., those due to indirect transitions, to direct transitions, and to creation of excitons. It does not seem possible to separate these contributions for GaSe under pressure, largely because of the proximity of the direct and indirect edges, but the existence of interference effects reinforces the notion that the lowest edge is an indirect one. Our belief in this model is further strengthened by the antiresonant behavior of the Raman tensor for different lattice modes, which has been observed recently, for variable excitation energies, in the region of the gaps.[18]

According to Ref. 9, the pressure coefficients of the gaps in GaS, GaSe, and GaTe are negative. Leaving aside GaTe for the course of this discussion, because of its different crystal structure, one notices that in the GaS_xSe_{1-x} series the gap increases[12] as the crystal parameter decreases with increasing x. A similar behavior might have been expected with increasing pressure, but the reverse is observed. This discrepancy may be resolved on the basis of recent band-structure calculations. The two conduction and valence bands at the center of the Brillouin zone originate from levels of the unperturbed two-dimensional layers which are split by interaction between the layers (Fig. 2). The splitting is comparatively large,[19,20] whereas interlayer bonding is small.[1,21,22] We can therefore expect the deformation potential along the c axis to be large, and the separation between the Γ_3^- and Γ_3^+ levels of the conduction band or that of the Γ_1^- and Γ_1^+ levels of the valence band to be much more sensitive to pressure than the energy difference of the unsplit Γ_3 and Γ_1 levels from which they originate (Fig. 2). The net result when pressure is increased will be a decrease of the energy difference of the Γ_3^+ and Γ_1^- levels forming the direct gap, thus giving a negative pressure coefficient.

GaS and GaSe may be expected to have similar pressure coefficients following an application of Paul's rule for levels of the same symmetry in isoelectronic and isostructural sequences which has been well verified up to now. The indirect gap of GaS has a pressure coefficient[9] of -13.5×10^{-6} eV/bar. This is quite different from the coefficient -6.5×10^{-6} eV/bar which we find for the low absorption tail of GaSe, or the value of -6.9×10^{-6} eV/bar which is proposed for the gap of GaSe.[9] The reason is that the measurements that we refer to here, ours and those of Ref. 9, have been made for the electric field of incident light perpendicular to the c axis of the crystal, $E\perp c$, where transitions are only weakly allowed by spin-orbit interaction. Indeed, evidence pointing to the presence of an indirect gap in GaSe has been obtained[4,5,13] only by spectra taken with $E\parallel c$. Therefore, the pressure coefficient of the indirect edge of GaSe must be that given by Niilisk and Kirs[9] for the photoconductive edge with $E\parallel c$ and the photocurrent in the c axis direction, that is, -13×10^{-6} eV/bar. With $E\perp c$, in our measurements and theirs, the indirect gap is too weak and too close to the direct exciton to be clearly separated from other contributions to the absorption coefficient. The coefficient of the low-energy tail represents the variation with pressure of several transitions: the shift of the direct gap, the broadening of the exciton line, and the appearance of indirect transitions.

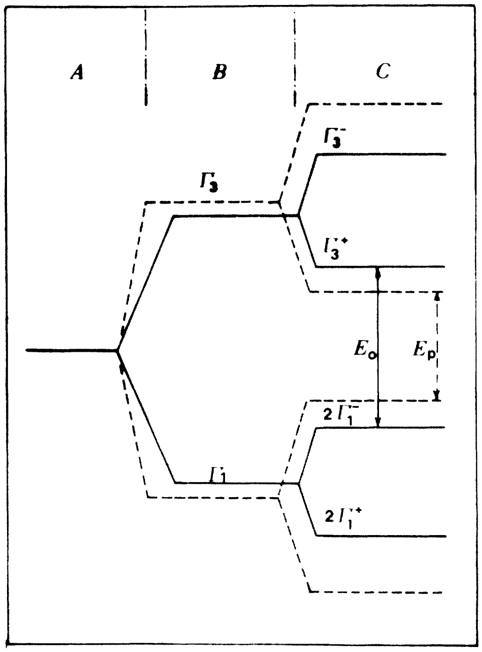

FIG. 2. Scheme of electronic levels at the Γ point in β-GaSe (after Ref. 19). Full lines: levels at room pressure; dashed lines: qualitative position of the levels after application of hydrostatic pressure. According to the chemical bond approach of Ref. 19, two plane hexagonal lattices of Ga and Se atoms are distorted along the c-axis direction, then bonded to form a layer. Layers are then brought together and interlayer interaction taken into account. Step A: Distorted hexagonal lattices without bonds; step B: bonding between two lattices included; step C: interaction between layers (β polytype).

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Study of Dispersive Raman Modes in Cu$_2$O by Resonant Raman Scattering

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We have observed shifts in energy of a number of Raman modes of Cu$_2$O as a function of incident photon energy. We explain such energy shifts as due to dispersion in the phonons involved and obtain quantitative agreement between theory and experiment. From our data we have also determined the effective mass of the 1*s* yellow exciton in Cu$_2$O to be $(3.0 \pm 0.2)m_0$.

It is generally accepted[1] that one-phonon Raman modes are characterized by zone-center phonons while multiphonon Raman modes reflect the phonon density of states near critical points. In either case for a given crystal orientation, the Raman frequency shift is independent of the exciting photon energy. In this Letter we report for the first time the observation of some Raman modes in Cu$_2$O whose frequencies vary with the exciting laser frequency. We have developed a theory to explain our results quantitatively and have shown that it is possible to obtain phonon dispersion relations and the effective mass of the 1*s* exciton band in Cu$_2$O by resonance Raman scattering (RRS).

Recently Yu *et al.*[2] have shown that RRS of the $2\Gamma_{12}^-$-phonon mode in Cu$_2$O[3] is dominated by the scattering process shown in Fig. 1(a). For a fixed incident photon energy ω_i, the momentum q of the Γ_{12}^- phonon emitted is determined uniquely