1-mm crystal at 77°K. A curve of signal versus temperature obtained with a 1-mm-thick crystal in this configuration is shown in Fig. 1. Note that this curve shows a much smaller signal at the phase-matching temperature than the corresponding curve with the large-radius mirror. The angular dependence of the output and the variation of the signal with temperature were shown to be very dependent upon the position of the crystal with respect to the horizontal and vertical focal lines of the off-axis mirror. A detailed treatment of this subject will be given separately.

Since the absorption at all three frequencies increases rapidly with temperature it is obviously preferable to phase match at a low temperature. A method of doing this in the collinear case using magnetoplasma effects has recently been described by Van Tran and Patel.[6] Since the index in the far infrared is larger than that in the near infrared, phase matching can also be obtained by having the input beams incident at a small angle to each other. In a first experiment utilizing this method a power in excess of 1 μW was obtained at 106 cm^{-1} by mixing two separate Q-switched CO_2 lasers incident at an angle, inside the crystal, of approximately 2° to each other. A full account of these experiments will be given at a later date.

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[1]F. Zernike, Bull. Am. Phys. Soc. 12, 687 (1967).
[2]C. K. N. Patel, Phys. Rev. Letters 17, 1011 (1966).
[3]W. J. Moore and H. Shenker, Infrared Phys. 5, 99 (1965).
[4]R. B. Sanderson, J. Phys. Chem. Solids 26, 803 (1965).
[5]F. Zernike and P. R. Berman, Phys. Rev. Letters 15, 999 (1965).
[6]N. Van Tran and C. K. N. Patel, Phys. Rev. Letters 22, 463 (1969).

STRESS-INDUCED EXCHANGE SPLITTING OF HYPERBOLIC EXCITONS IN GaAs.*

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Evidence for the existence of hyperbolic excitons has been obtained from a study of the effects of compressive uniaxial stresss on optical structure of GaAs at 77°K using a double-beam wavelength-modulation technique. We have observed a polarization-dependent splitting of this structure which cannot be accounted for on the basis of one-electron band theory but is explained by including the electron-hole exchange interaction. An estimate of an effective radius of ≈10 Å for the electron-hole interaction has been made.

The existence of significant contributions of the electron-hole Coulomb interaction (i.e., exciton effects) to the experimental optical spectra in the vicinity of M_1 (hyperbolic) interband transitions [for example, the E_1-$(E_1+\Delta_1)$ structure in diamond- and zinc-blende-type semiconductors] has been suggested by several authors.[1-6] The experimental evidence is not conclusive although a recent study of the wavelength derivative spectra of the E_1-$(E_1+\Delta_1)$ structure in InSb strongly suggests that the electron-hole Coulomb interaction must be taken into account.[7] In this paper we present conclusive evidence for the existence of hyperbolic excitons based on symmetry considerations and not dependent on interpretations of line shape.[7] The E_1-$(E_1+\Delta_1)$ structure of GaAs has been studied as a function of static uniaxial compression along [100] at 77°K using a double-beam wavelength-modulation technique. One-electron band theory predicts that no splitting for this optical structure should occur for [100] stress since for this stress direction the valley degeneracy is not changed[8] and stress does not remove the Kramers' degeneracy.[9] However, a small polarization-dependent splitting is observed and is explained by including the electron-hole exchange interaction as well as the one-electron deformation potential. From these measurements the effective radius for the electron-hole interaction is estimated to be ≈10 Å.

Several optical-modulation methods (e.g., electroreflectance,[10,11] piezoreflectance[12]) have been used to study critical-point structure in the optical spectra of semiconductors. Of these methods, wavelength-modulated reflectance (WMR) is particularly attractive from a theoretical

point of view since the interpretation of these experiments involves only the theory of the optical properties of the unperturbed sample and not that of the effect of the perturbation on the optical properties. We have used WMR to study the effect of a static uniaxial compression along the [100] direction on the E_1-$(E_1+\Delta_1)$ doublet in n-type GaAs[13] ($n=1.1\times10^{16}$ cm^{-3}). The WMR was measured on a [110] face which had been polished and etched by conventional procedures. The stress apparatus has been previously described.[14]

Figure 1 shows the stress dependence of the E_1 and $E_1+\Delta_1$ transitions measured at 77°K for a [100] stress direction. The filled (open) circles correspond to the electric vector of the incident light polarized perpendicular (parallel) to the stress axis. It can be seen that each transition is split equally by the stress with the higher energy component of E_1 occurring for the parallel polarization while the higher energy $E_1+\Delta_1$ component occurs for the perpendicular polarization. A similar splitting and polarization pattern has been observed by Koda and Langer[15] for parabolic excitons in hexagonal ZnO, CdS, and CdSe which they interpret as due to the two-particle nature of the exciton state (i.e., Kramers' degeneracy is not required for two-particle states). More recently Akimoto and Hasegawa[16] have shown that the combined effect of uniaxial stress and the electron-hole exchange interaction is responsible for the splitting and polarization of parabolic excitons in these II-VI compounds. Hence we anticipate that similar considerations apply for the E_1-$(E_1+\Delta_1)$ doublet in GaAs.

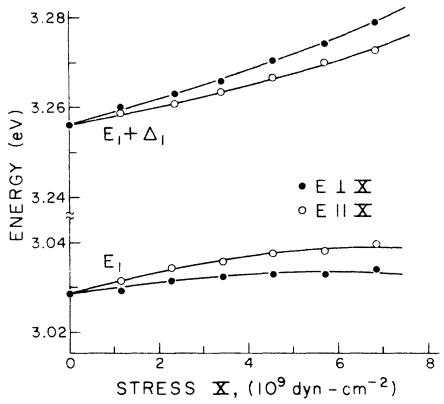

FIG. 1. The stress dependence of the E_1 and $E_1+\Delta_1$ optical structure of GaAs at 77°K for stress along [100]. The filled (open) circles correspond to the electric field vector of the incident light polarized perpendicular (parallel) to the stress axis.

In the present case the valence and conduction bands are Λ_{6v}, $\Lambda_{4,5v}$, and Λ_{6c} states,[17] respectively, of the irreducible representations of the double C_{3v} group of the wave vector $\vec{k}\|[111]$. Exciton states belong to single-group representations and are generated by the direct product of the valence- and conduction-band representations. Here the exciton states are

$$E_1:\ \Lambda_{4,5v}\times\Lambda_{6c}=2\Lambda_3, \tag{1}$$

$$E_1+\Delta_1:\ \Lambda_{6v}\times\Lambda_{6c}=\Lambda_1+\Lambda_2+\Lambda_3, \tag{2}$$

under the operation of the corresponding C_{3v} group. Consideration of only this symmetry is sufficient provided that the valley-orbit interaction is neglected. Of these states only two of the twofold Λ_3 excitons interact strongly with light since the formation of the other states involves spin flip. Hence we restrict our attention to these "allowed" states which can be written as

$$E_1:\ \varphi_1=|2^{-1/2}(x+iy)\alpha_h\beta_e\rangle,$$

$$\varphi_2=|2^{-1/2}(x-iy)\beta_h\alpha_e\rangle,$$

$$E_1+\Delta_1:\ \varphi_3=|2^{-1/2}(x+iy)\beta_h\alpha_e\rangle,$$

$$\varphi_4=|2^{-1/2}(x-iy)\alpha_h\beta_e\rangle, \tag{3}$$

where α and β are the usual spin-up and -down functions, and we have chosen z as the threefold symmetry axis. Envelope functions (which describe the relative orbital motion of the electron-hole pair) are omitted from Eq. (3) since for allowed optical transitions they commute with the strain Hamiltonian and hence contribute only a scale factor to the matrix elements.[18] The energy dependence of the envelope function for $r=0$ is the dominant factor in determining the exciton line shape. The interpretation of the present experiments in terms of hyperbolic excitons is based solely on symmetry and does not depend on the knowledge of the envelope function.[4,6]

By taking symmetric and antisymmetric linear combinations of the pair (φ_1, φ_2) or (φ_3, φ_4) we obtain states polarized in the x and y directions,[19] respectively. The combined exchange and strain

Hamiltonian in this new basis has the form

$$\begin{array}{cccc} \Lambda_{3x}^{E_1} & \Lambda_{3x}^{E_1+\Delta_1} & \Lambda_{3y}^{E_1} & \Lambda_{3y}^{E_1+\Delta_1} \\ \begin{bmatrix} E_1+\delta_H & \sigma_j-\delta_S & 0 & 0 \\ \delta_j-\delta_S & E_1+\Delta_1+\delta_H & 0 & 0 \\ 0 & 0 & E_1+\delta_H & \delta_J+\delta_S \\ 0 & 0 & \delta_J+\delta_S & E_1+\Delta_1+\delta_H \end{bmatrix} & , \end{array} \tag{4}$$

where δ_H, δ_S, and δ_J are matrix elements due to hydrostatic strain, shear strain, and electron-hole exchange, respectively. We neglect the strain dependence of the exchange potential. According to Elliott[20] the exchange term can be written

$$\delta_J = P(0)J, \tag{5}$$

where $P(0)$ is the probability that the electron and hole are on the same lattice site and J is the exchange integral between Wannier functions. The strain terms are

$$\delta_H = \mathcal{E}_1(S_{11}+2S_{12})X, \tag{6}$$

and

$$\delta_S = b(S_{11}-S_{12})X, \tag{7}$$

where $\mathcal{E}_1$[21,22] and b[8,23] are the one-electron deformation potentials, S_{ij} are the elastic compliance constants, and X is magnitude of the stress. Since a [100] stress affects all [111] directions equally, the summation over equivalent valleys is trivial provided one neglects valley-orbit splitting.[24] The observed selection rules[25] agree with Eq. (4) and hence rule out a splitting due only to valley-orbit effects. A consideration of valley-orbit effects based on the Kohn-Luttinger theory (see Ref. 24) indicates that singlet states make the dominant contribution to electric-dipole transitions. For strong valley-orbit splitting both E_1 and $E_1+\Delta_1$ should appear as doublets since there are two singlet states. The doublet components will split equally under [100] stress due to the combined effect of strain and exchange. Since these valley-orbit-split doublets are not resolved experimentally, the observed peak corresponds to the "center of gravity" which has the same stress dependence and selection rules as in the case of no valley-orbit splitting.

We write the exciton energies [found by solving Eq. (4)] as

$$E = E_1+\delta_H+\tfrac{1}{2}\Delta_1 \pm [(\tfrac{1}{2}\Delta_1)^2+(\delta_J \pm \delta_S)^2]^{1/2}. \tag{8}$$

To the first order in the applied stress we have

$$E = E_1+\delta_H+\tfrac{1}{2}\Delta_1 \pm [\tfrac{1}{2}\Delta_1 \pm \delta], \tag{9}$$

$$\delta = 2\frac{P(0)Jb}{\Delta_1}(S_{11}-S_{12})X. \tag{10}$$

We define an effective radius, a_X, for these hyperbolic excitons[20] by

$$P(0) = a_l^3/\pi a_X^3, \tag{11}$$

where a_l is the lattice constant. Using the results of Fig. 1 and the known values of b, S_{11}, S_{12}, and a_l as well as the assumption $J \approx \Delta_1$ we obtain $a_X \approx 10$ Å. This value of a_X should give an estimate of the range of the electron-hole interaction at hyperbolic critical points.

In addition to the splitting (see Fig. 1) large polarization-dependent intensity changes were observed due to wave function mixing by the off-diagonal matrix elements of Eq. (4). A discussion of the stress dependence of these intensities as well as the values obtained for one-electron deformation potentials will be presented in a later publication.

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[1]J. C. Phillips, Solid State Phys. 18, 56 (1966).

[2]M. Cardona and G. Harbeke, J. Appl. Phys. 34, 813 (1963).

[3]B. Velický and J. Sak, Phys. Status Solidi 16, 147 (1966).

[4]C. Duke and B. Segall, Phys. Rev. Letters 17, 19 (1966).
[5]Y. Toyozawa, M. Inoue, T. Inoui, M. Okazaki, and E. Hanamura, Proc. Phys. Soc. Japan Suppl. 21, 133 (1967).
[6]E. O. Kane, Phys. Rev. (to be published).
[7]K. L. Shaklee, J. E. Rowe, and M. Cardona, Phys. Rev. 174, 828 (1968).
[8]F. H. Pollak and M. Cardona, Phys. Rev. 172, 816 (1968).
[9]If there is a stress-dependent term in the spin-orbit Hamiltonian, an intravalley splitting of the [111] Bloch states is possible in the zinc-blende structure. However, the selection rules associated with this splitting are incompatible with the experimental observations reported here.
[10]M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).
[11]B. O. Seraphin and N. Bottka, Phys. Rev. 145, 628 (1966).
[12]G. Gobeli and E. O. Kane, Phys. Rev. Letters 15, 142 (1965).
[13]Obtained from Bell and Howell Research Center, Pasadena, Calif. 91109.
[14]See Ref. 8 and M. Cuevas and H. Fritzsche, Phys. Rev. 137, A1847 (1965); F. H. Pollak, ibid. 138, A618 (1965).
[15]T. Koda and D. W. Langer, Phys. Rev. Letters 20, 50 (1968).
[16]O. Akimoto and H. Hasegawa, Phys. Rev. Letters 20, 916 (1968).
[17]D. Brust, Phys. Rev. 134, A1337 (1964); M. L. Cohen and T. K. Bergstresser, ibid. 141, 789 (1966).
[18]E. O. Kane, Phys. Rev. 178, 1368 (1969).
[19]These states have the electric-dipole selection rules: The Λ_{3x} states are allowed only for the x polarization and the Λ_{3y} states are allowed only for the y polarization. Since the spin terms in each pair are different the above states do not factor into a product of a spin term and an orbital term with x (y) symmetry.
[20]R. J. Elliot, Phys. Rev. 108, 1384 (1959).
[21]H. Brooks, Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 85.
[22]We have used script $\mathcal{E}$ to indicate the deformation potential in order to avoid confusion with the symbol used for the optical structure.
[23]G. E. Picus and G. L. Bir, Fiz. Tverd. Tela 1, 154 (1959), and 1, 1642 (1959) [translations: Soviet Phys. -Solid State 1, 136 (1959), and 1, 1502 (1960)]; G. E. Picus, ibid. 6, 324 (1963) [translation: Soviet Phys. -Solid State 6, 261 (1964)].
[24]W. Kohn, Solid State Phys. 5, 257 (1957); H. Fritzsche, Phys. Rev. 125, 1560 (1962). Valley-orbit effects should be weaker for excitons than for impurity states because the charge distribution of the hole is usually not as localized as the central cell potential of an impurity.
[25]Due to the fact that the stress axis is not orthogonal to any of the [111]-type valleys the polarization selection rules are not complete. In the present experiment the mode $E \| X$ consisted only of Λ_{3y} states, but the mode $E \perp X$ consisted of $\frac{3}{4}\Lambda_{3x}$ and $\frac{1}{4}\Lambda_{3y}$. It is clear that the experimental peak energy corresponds to Λ_{3x} for $E \perp X$ while the admixture of Λ_{3y} contributes to line broadening.

THEORY OF ELECTRONIC SWITCHING EFFECT AS A COOPERATIVE PHENOMENON*

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A modified form of Zener tunneling theory, in which we assume that the tunneling barrier is a decreasing collective function of electronic excitation, is shown to imply insulator-to-metal switching characteristics similar to those reported by Ovshinsky for glass film devices. In addition, our I-V characteristics display a region of negative resistance. Some criteria for the existence of polyconductivity are discussed, and are shown to be met by several classes of material.

A phenomenon recently reported by Ovshinsky[1] concerning the reversible switching of glassy thin films from the insulating to the conducting state, which we here denote "polyconductivity," is sufficiently startling to warrant speculative theoretical investigation. We wish to report here the results of one such speculation: Zener tunneling theory seems capable of explaining the unusual insulating-state characteristics of Ovshinsky's devices provided it is assumed that the tunneling barrier E_g is a decreasing function of the degree of electronic excitation. It is possible then that the switching properties are a new manifestation of the Mott transition.[2]

The set of equations which is discussed below was solved numerically by the present author in close collaboration with L. Landovitz and M. Plischke. Some interesting results obtained by the three of us are displayed graphically herewith. If our basic hypotheses are correct, these results imply that the glass devices should be characterized by a figure of merit which we have denoted