563 (1969).
[11]G. R. Cook and B. K. Ching, J. Chem. Phys. 43, 1794 (1965).
[12]R. W. Kiser and D. L. Hobrock, J. Amer. Chem. Soc. 87, 922 (1965).
[13]D. W. Davies, Chem. Phys. Lett. 2, 173 (1968).
[14]K. Dressler, private communication.
[15]J.-Y. Roncin, J. Mol. Spectrosc. 26, 105 (1968).
[16]S. C. Greer and L. Meyer, J. Chem. Phys. 51, 4583 (1969).
[17]E. Boursey, J.-Y. Roncin, and N. Damany, Chem. Phys. Lett. 5, 584 (1970).
[18]R. A. H. Buxton and W. W. Duley, Phys. Rev. Lett. 25, 801 (1970).
[19]S. R. Sharber and S. E. Webber, to be published.
[20]G. C. Morris and J. G. Angus, to be published.

New Analysis of Direct Exciton Transitions: Application to GaP

D. D. Sell and P. Lawaetz
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 23 November 1970)

A new analysis of direct exciton data is presented and applied to the $E_0, E_0+\Delta_0$ transitions in GaP. A curve-fitting procedure is used to compare both the discrete and continuum structure in the data with theoretical curves. Good agreement is obtained for the binding energies, broadening, strengths, and shapes. It is shown that the binding energy of E_0 is 11 ± 1 meV rather than the 5-6–meV value previously obtained from the conventional analysis.

We have reexamined the absorption data of Dean, Kaminsky, and Zetterstrom[1] for the direct exciton (E_0) and the spin-orbit split-off exciton ($E_0+\Delta_0$) in GaP. In our new analysis the exciton binding energy and the broadening are determined from a comparison of the data with the theoretical spectrum including both the discrete and continuum contributions. We show that the experimental shapes, strengths, and binding energies of these excitons are well accounted for by recent refinements[2] of the simple Wannier exciton theory.[3] A new value of 11 meV is obtained for the E_0 exciton binding energy which is considerably larger than the previous estimates of 5-6 meV.[1,4] We believe that our results convincingly demonstrate that this new, but yet very basic, method of analysis can provide a stringent comparison between theory and experiment.

The 25-K absorption data of Dean, Kaminsky, and Zetterstrom[1] are shown as the solid curve in Fig. 1. This structure results from electronic transitions from the highest valence band to the lowest conduction band near $k=0$. The splitting between E_0 and $E_0+\Delta_0$ is caused by the well-known spin-orbit splitting of the six valence states into a fourfold (E_0) and a twofold ($E_0+\Delta_0$) degenerate state at $k=0$. In addition to these direct transitions, we estimate that indirect transitions ($\Gamma\rightarrow X$) contribute a rather flat background absorption of approximately 1000 cm^{-1} in this region.

The $E_0+\Delta_0$ structure is an example of the well-known "textbook" case of a Wannier exciton with a hydrogenic series of discrete levels with energies

$$E_n=E_g-\mu e^4/2\epsilon_s{}^2\hbar^2n^2=E_g-R_0{}^*/n^2, \quad (1)$$

where E_g is the band gap, μ is the reduced mass [$\mu^{-1}=m_c{}^{*-1}+m_{s.o.}{}^{*-1}$ for the conduction ($m_c{}^*$) and split-off ($m_{s.o.}{}^*$) bands], ϵ_s is the static dielectric constant, and $R_0{}^*$ is the effective Rydberg. The total absorption coefficient (for no broadening) consists of the discrete lines (among which the $1s$ state predominates) plus the exciton

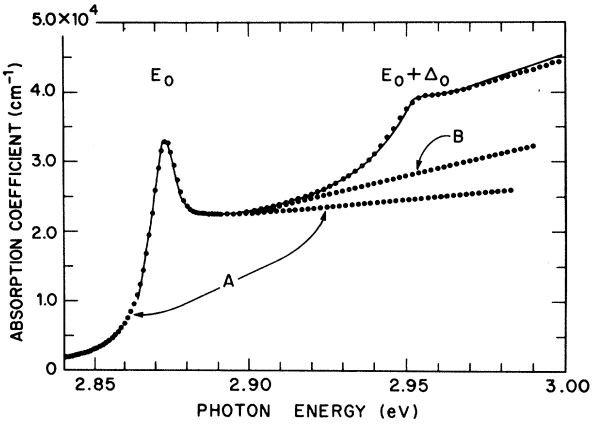

FIG. 1. Direct E_0 and $E_0+\Delta_0$ exciton absorption of GaP at 25 K. The solid curve is the data of Dean, Kaminsky, and Zetterstrom, Ref. 1. The dotted curves are the various theoretical fits discussed in the text.

continuum[3]:

$$\alpha(E)=\frac{(2\mu)^{3/2}e^2f_{cv}}{Nc\hbar^2m_0}\left[\sum_n 4\pi {R_0}^{*3/2}\frac{\delta(E-E_n)}{n^3}+\frac{2\pi {R_0}^{*1/2}u(E-E_g)}{1-e^{-2\pi Z}}\right], \tag{2}$$

where f_{cv} is the oscillator strength, N is the refractive index (at energy E), m_0 is the free electron mass, $Z^2={R_0}^*/(E-E_g)$, and $u(x)$ is the unit step function.

To obtain realistic curves which can be compared with experiment we convolute $\alpha(E)$ with a Lorentzian function $\Gamma\pi^{-1}(E^2+\Gamma^2)^{-1}$, where Γ is the half width at half-maximum of the Lorentzian and the associated lifetime is $(2\Gamma)^{-1}$. The resulting broadened absorption profiles for various values of $G=\Gamma/{R_0}^*$ are shown in Fig. 2. Here a normalized energy scale has been used such that ${R_0}^*=\frac{1}{2}$, and the terms within the square brackets in Eq. (2) are used for the unbroadened absorption coefficient. These broadened curves form the basis for our comparison of theory and experiment. These curves and their counterparts ϵ_1, ϵ_2, $d\epsilon_1/dE$, and $d\epsilon_2/dE$ are also useful for studies concerned directly with the broadening mechanisms for optical structure. This will be discussed elsewhere.[5]

The E_0 exciton is not a "textbook" case (even though it is often treated as one) because of the light-heavy-hole band degeneracy. Baldereschi and Lipari[2] have recently developed a perturbation method to obtain the $1s$ and $2s$ energy levels of the fourfold-degenerate E_0 exciton. From their results and from our estimate of similar effects of degeneracy upon the continuum states, we conclude that for GaP, Eqs. (1) and (2) can also be used (with an accuracy of approximately 2%) to describe the E_0 excitons if two modifications are made: (1) Equation (2) must be multiplied by a factor of 2 to account for the additional degeneracy, and (2) an effective reduced mass μ must be used.[6] For GaP, this effective reduced mass is approximately 10% greater than the simple isotropic light- and heavy-hole average (μ_0 of Ref. 2). From another point of view, the good fit which we obtain for E_0 also justifies the use of Eq. (2) to describe the E_0 absorption.

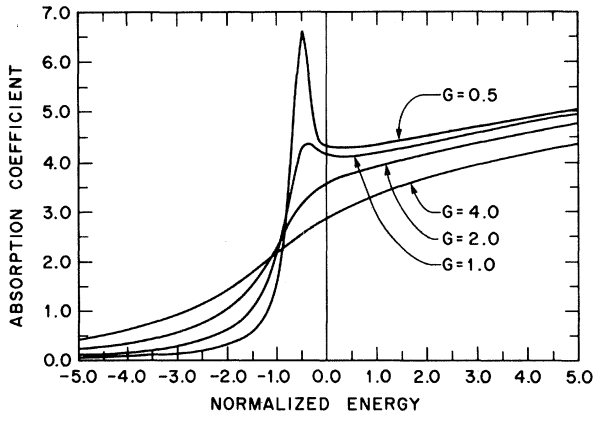

FIG. 2. Theoretical exciton-absorption curves for several values of the broadening parameter $G=\Gamma/{R_0}^*$. The units are such that the $1s$-exciton binding energy is -0.5. The absorption strength at the band gap ($=0.0$) is $\sqrt{2}\pi$.

A linear least-squares curve-fitting procedure has been used to compare the theoretical and experimental curves:

$$\alpha\cong C_1\alpha_T(\Gamma,{R_0}^*)+C_2, \tag{3}$$

where α denotes the data, $\alpha_T(\Gamma,{R_0}^*)$ denotes the broadened theoretical curve for a given value of Γ and ${R_0}^*$, and C_1 and C_2 are the coefficients which give the best fit. The constant term C_2 is included to account for the background and is expected to be realistically small ($\lesssim 10^3$ cm^{-1}). The parameters Γ and ${R_0}^*$ are then varied to obtain the best fit to the data, i.e., to minimize the rms error. This procedure can be handled in a rather simple, straightforward manner on a digital computer.

The results of this curve fitting are shown in Fig. 1 and are tabulated in Table I. The dotted curve marked A is obtained for ${R_0}^*=11$ meV, $\Gamma=6$ meV ($G=0.54$). The curve fitting has been carried out over the energy interval 2.864 to 2.890 eV which includes the exciton peak and the beginning of the continuum. Since the fit for $E_B=10$ or 12 meV is noticeably worse, we are quite confident that the binding energy is ${R_0}^*=11\pm1$ meV and that previous estimates[1,4] of ${R_0}^*\sim 5$-6 meV are incorrect.

The reason why the previous value is too small is clear from Fig. 1. In the earlier work the binding energy was determined from the slope of the continuum in the 2.89- to 2.92-eV region. We find, however, that this slope has contributions from three sources: the continuum of E_0, the broadened leading structure of $E_0+\Delta_0$, and the effects of nonparabolicity (discussed below). Thus the slope of the data is considerably greater than that of curve A which represents the E_0-exciton continuum for parabolic bands.

Now let us consider the $E_0+\Delta_0$ structure. This

Table I. Comparison between experimental and theoretical values. The following parameters were used: $m_0/m_c^*=5.8$,[a] $m_0/m_{s.o.}^*=4.13$,[a] $\gamma_1=4.20$,[a] $\gamma_2=0.98$,[a] $\gamma_3=1.66$,[a] $f_{cv}=5.1$,[a] $N=4.0$,[b] $\epsilon_s=10.75$.[c]

	E_0		$E_0+\Delta_0$	
	Expt.	Theory	Expt.	Theory
m_0/μ		9.17		9.93
R_0^* (meV)	11 ± 1	12.8	10 ± 2	11.9
Γ (meV)	6 ± 1	...	12 ± 2	14
E_g (eV)	2.884 ± 0.001	...	2.962 ± 0.002	...
$\alpha(E_g)$ (cm^{-1})	21700	24400	10200	10200

[a]Ref. 8.
[b]Extrapolated from values in Ref. 1.
[c]Ref. 11.

case is more complicated than E_0 because of the large background from E_0 and because the broader line shape is not as distinctive. As a first approach, assume that curve A represents the E_0 continuum and subtract it from the original data to obtain the α of Eq. (3) for $E_0+\Delta_0$. The values $R_0^*=10$ meV and $\Gamma=12$ meV give a reasonably good fit (not shown in Fig. 1) except that the slope of the theoretical continuum curve is less than that of the data in the 2.98-eV region. A related problem is that the overall strength of the absorption of approximately 14000 cm^{-1} at the band gap (2.962 eV) is somewhat larger than the value 10200 cm^{-1} obtained from Eq. (2) for reasonable parameters.

We believe that the answer to both of these problems is that the valence bands are quite nonparabolic as was pointed out by Wiley and DiDomenico.[7] For increasing k vector the light- and heavy-hole masses tend to increase. This tends to increase the slope of the E_0-continuum background. Since it is difficult to calculate the effect of the nonparabolicity, we have attempted to account for it in the following way. Starting at 2.90 eV, the linear background curve B has been introduced with a slope such that the $E_0+\Delta_0$ amplitude is 10200 cm^{-1}, the theoretical value, at 2.962 eV. For this background, the fit to $E_0+\Delta_0$ shown in Fig. 1 is obtained for the parameters $R_0^*=10$ meV and $\Gamma=11$ meV. It is seen that the binding energy is not particularly sensitive to the choice of background, but that the broadening parameter is somewhat smaller for curve B than for curve A. Thus for the split-off band we conclude $R_0^*=10\pm2$ meV, $\Gamma=12\pm2$ meV. This is the first experimental value for the $E_0+\Delta_0$ binding energy in GaP.

Our results are compared with theoretical values in Table I. The theoretical binding energies were obtained from the appropriate expressions in Ref. 2 using the mass parameters calculated by Lawaetz[8] which are given in Table I. The absorption strengths at the band gaps were calculated from Eq. (2). It is seen that the agreement is generally quite good. The small discrepancies between experimental and theoretical binding energies are probably caused by exchange effects[9] which tend to lower the binding energy of the observed 1s excitons. It will be shown elsewhere[5] that it is also possible to account for the additional width of $E_0+\Delta_0$ relative to E_0 in terms of nonpolar optical scattering of the holes in the split-off valence band into the upper valence bands. Thus, the shape, strength, and binding energy of both excitons as well as the width of $E_0+\Delta_0$ are all accounted for. The width of E_0 is the only experimental quantity that is not compared with theory (the difficulty being that the conduction-band density of states is not accurately known for large values of k). Our results indicate a spin-orbit splitting parameter $\Delta_0=78\pm2$ meV as the energy separation between the band edges.

Finally, it is worthwhile to compare the present analysis with two previous approaches. One of these concentrates upon the discrete lines of Eqs. (1) and (2). If these lines are resolved, their energy separation can be used to determine R_0^*. The other approach concentrates upon the slope of the continuum term in Eq. (2) to determine R_0^*. The advantage of our approach is that it makes use of both the discrete and continuum data and provides a more stringent test of theory. We have shown here that the continuum-slope method can give rather erroneous results. Another example of this is that the continuum-slope method tends to predict for both GaP[4] and GaAs[10] that R_0^* decreases as the temperature increases. From Fig. 2 it can be seen that the ad-

ditional broadening at higher temperatures must be taken into account.

We gratefully thank E. O. Kane for several helpful discussions and for providing the computer program used to calculate the curves in Fig. 2, and P. J. Dean for allowing us to use his original data.

[1]P. J. Dean, G. Kaminsky, and R. B. Zetterstrom, J. Appl. Phys. 38, 3551 (1967).
[2]A. Baldereschi and N. O. Lipari, Phys. Rev. Lett. 25, 373 (1970); N. O. Lipari and A. Baldereschi, Phys. Rev. Lett. 25, 1660 (1970).
[3]R. J. Elliott, Phys. Rev. 108, 1384 (1957).
[4]V. K. Subashiev and G. A. Chalikyan, Phys. Status Solidi 13, K91 (1966).
[5]D. D. Sell and P. Lawaetz, to be published.
[6]See Eq. (6) of the first paper in Ref. 2.
[7]J. D. Wiley and M. DiDomenico, Phys. Rev. B 2, 427 (1970).
[8]P. Lawaetz, to be published.
[9]Y. Abe, J. Phys. Soc. Jap. 19, 818 (1964); T. Skettrup and I. Balslev, Phys. Status Solidi 40, 93 (1970).
[10]M. D. Sturge, Phys. Rev. 127, 768 (1962).
[11]L. Patrick and P. J. Dean, Phys. Rev. 188, 1254 (1969).

Effect of a Vacancy on the Jahn-Teller-Distorted Γ_4^- Excited States in KI:Sn^{2+} as Observed in Polarized Luminescence*

Atsuo Fukuda†
Argonne National Laboratory, Argonne, Illinois 60439
(Received 14 December 1970)

Four emission bands related to the A and C excited states, $A_{T\Pi}$, $A_{T\Sigma}$, $C_{T\Sigma}$, and $C_{T\Pi}$, have been observed in KI:Sn^{2+} at 4.2°K, and the degree of polarization has been studied. The results indicate that the Γ_4^- ($^3T_{1u}$ and $^1T_{1u}$) excited states are tetragonally distorted by a strong Jahn-Teller effect and are also perturbed by a charge-compensating vacancy located in the nearest-neighbor position.

The $^3T_{1u}$ and $^1T_{1u}$ ($a_{1g}t_{1u}$) excited states of Tl^+-type centers in alkali halides are characterized by a strong Jahn-Teller effect (JTE).[1] Most investigators[1-8] believe that the polarized luminescence from the monovalent impurity-ion (Tl^+, In^+, and Ga^+) centers is caused by the JTE. However, many of them[8-12] still believe that the polarized luminescence from the divalent impurity-ion (Pb^{2+} and Sn^{2+}) centers is mainly due to a charge-compensating vacancy; they have considered the effect of the vacancy to be more important than the JTE. The analysis of the absorption-band shape has, however, shown that the JTE in the divalent impurity-ion centers is much stronger than in the monovalent ones.[13-15] In this Letter we report the polarization spectra of luminescence from the Γ_4^- ($^3T_{1u}$ and $^1T_{1u}$) excited states in KI:Sn^{2+} at 4.2°K, which clearly demonstrate a strong JTE and an effect due to the vacancy that is weaker than the JTE. Luminescence was observed with an EMI 9558QB photomultiplier after being dispersed by a single-grating monochromator; excitation was accomplished with a xenon lamp in combination with a double-prism monochromator. Sample crystals were always quenched from 650°C onto an aluminum foil at room temperature.

Excitation in the A absorption band produces two emission bands, $A_{T\Pi}$ (2.23 eV) and $A_{T\Sigma}$ (2.40 eV); the ratio of intensities between them depends on the photon energy of the exciting light.[1] The degree of polarization for $A_{T\Pi}$ or $A_{T\Sigma}$,

$$P=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp}),$$

depends on the direction of polarization and the photon energy of the exciting light, where $I_{\parallel}$ and $I_{\perp}$ are the intensities of $A_{T\Pi}$ or $A_{T\Sigma}$ polarized parallel and perpendicular to the direction of polarization of the exciting light, respectively. We used the exciting light incident upon the (100) plane perpendicularly so that the direction of polarization is specified by the azimuthal angle α in the (100) plane. The degrees of polarization $P(\alpha;A_{T\Pi})$ and $P(\alpha;A_{T\Sigma})$ as functions of α have a maximum at $\alpha=0°$ and 90° (in the [001] and [010] directions) and become zero at $\alpha=\pm45°$ (in the [011] and [0$\bar{1}$1] directions), irrespective of the photon energy of exciting light, $\hbar\omega$. In Fig. 1 are shown the degrees of polarization $P(\hbar\omega;A_{T\Pi})$ and $P(\hbar\omega;A_{T\Sigma})$ as functions of $\hbar\omega$ (the polarization spectra) at $\alpha=0°$ for $A_{T\Pi}$ and $A_{T\Sigma}$. Characteristic features are as follows: (A1) $P(\hbar\omega;A_{T\Pi})$ is