find that the quantizing component of the magnetic field is just that which threads the real space orbit, and that aside from a possible but unobserved small change in the ground state energy, the component of the field that is in the plane of the 2DEG does not significantly effect the behavior of the electrons. We have established that the effective mass for electrons moving parallel to the surface is the same as in the bulk, independent of the direction of the applied magnetic field. The fact that the Landé g value is substantially larger than the bulk value and depends on the density of the surface electrons remains to be quantitatively accounted for.

We wish to acknowledge the many helpful discussions we had with A. B. Fowler, W. E. Howard, Jr., F. Stern, and J. Janak. We herewith acknowledge the valuable technical assistance of J. Cummings.

PHYSICAL REVIEW VOLUME 174, NUMBER 3 15 OCTOBER 1968

New Evidence for the Existence of Exciton Effects at Hyperbolic Critical Points*

KERRY L. SHAKLEE,† J. E. ROWE, AND MANUEL CARDONA‡
Department of Physics, Brown University, Providence, Rhode Island 02912
(Received 22 April 1968)

The derivative of the reflectivity spectrum of InSb near the E_1 and $E_1+\Delta_1$ peaks has been measured at 77°K with a double-beam wavelength-modulation method which emphasizes singularities in the dielectric constant, $\epsilon_1(\omega)+i\epsilon_2(\omega)$. The experimental line shapes of $d\epsilon_1/d\omega$ and $d\epsilon_2/d\omega$ cannot be explained as being due to the generally accepted M_1 (hyperbolic) critical points, but are intermediate between the line shapes for M_1 and M_2 critical points. This mixture of line shapes is, in view of our knowledge of the one-electron band structure of InSb, evidence for the contribution of the electron-hole interaction (exciton effects) to the observed optical spectra.

THE existence of a significant contribution of the electron-hole Coulomb interaction (i.e., exciton effects) to the experimental optical spectra in the vicinity of M_1 interband critical points has been suggested by several authors.[1,2] However, the experimental evidence available so far is not conclusive, and the situation is further complicated by difficulties in the theoretical treatment of this exciton problem.[3,4] The purpose of this paper is to show that wavelength-derivative spectra of transitions near M_1 critical points in zincblende-type semiconductors, coupled with the present knowledge of the band structure of these materials, constitutes strong evidence for the importance of the electron-hole Coulomb interaction in the vicinity of M_1 critical points.

The usefulness of optical-modulation methods for studying the nature of interband critical points has been emphasized by many authors.[5–7] These methods extract the critical-point structure from the large, uniform background and thus yield a more detailed picture of the singular line shape. Techniques which modulate the optical properties of the sample (e.g., electroreflectance[5,7]) are particulaly simple from an experimental point of view, since any structure due to the spectral dependence of the light-source intensity, optical system, or detector response is easily eliminated. However, the interpretation of these sample modulation experiments requires a theoretical description of both the optical properties of the sample and the effect of the modulating perturbation on these properties. The theoretical treatment of the modulation is especially complicated in cases where the perturbation destroys the translational invariance of the crystal (such as electroreflectance[8]). These difficulties in interpretation are obviated by using a wavelength-derivative method at the expense of experimental simplicity; a suitable double-beam system must be used to eliminate the derivative structure due to the spectral dependence of the source, optical system, and detector.

We have developed a sensitive double-beam wavelength-modulation spectrometer which eliminates most of the difficulties usually encountered in this technique.[9] The modulation of the wavelength is produced by a rotationally vibrating quartz plate[10] placed in the entrance

* Supported by the Advanced Research Projects Agency and the National Science Foundation.
† Corina Borden Keene University Fellow.
‡ Alfred P. Sloan Foundation Research Fellow.
[1] J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 56.
[2] M. Cardona and G. Harbeke, J. Appl. Phys. **34**, 813 (1963).
[3] C. Duke and B. Segall, Phys. Rev. Letters **17**, 19 (1966).
[4] B. Velický and J. Sak, Phys. Status Solidi **16**, 147 (1966).
[5] B. O. Seraphin and N. Bottka, Phys. Rev. **145**, 628 (1966).
[6] G. Gobeli and E. O. Kane, Phys. Rev. Letters **15**, 142 (1965).
[7] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. **154**, 696 (1967).
[8] D. E. Aspnes, Phys. Rev. **153**, 972 (1967).
[9] G. Bonfiglioli and P. Brovetto, Appl. Opt. **3**, 1417 (1964); G. Bonfiglioli, P. Brovetto, G. Busca, S. Levialdi, G. Palmieri, and E. Wanke, *ibid.* **6**, 447 (1967).
[10] R. E. Drews, Bull. Am. Phys. Soc. **12**, 384 (1967).

beam of the monochromator. The details of the experimental arrangement are discussed elsewhere.[11]

Figure 1(a) shows the experimentally obtained logarithmic derivative of the reflectivity spectrum for InSb at 77°K near the $E_1-E_1+\Delta_1$ doublet, and in Fig. 1(b) is shown the conventional reflectivity spectrum obtained by numerical integration of $R^{-1}dR/d\omega$. The spectrometer used had a resolution of 5 Å and a peak-to-peak modulation of 7 Å. The sharp structure in the derivative spectrum at 1.9 and 2.4 eV would be difficult to resolve by conventional reflectivity techniques, since these are limited in sensitivity to $\sim 0.1\%$. The large negative peaks in $R^{-1}dR/d\omega$ are strongly temperature-dependent, and decrease in intensity by a factor of 3 in going from 77 to 300°K. Similar spectra have been obtained for Ge, GaAs, and HgTe for the E_1 and $E_1+\Delta_1$ transitions, indicating that this effect is characteristic of all members of the diamond-zincblende semiconductor family.

In order to compare the experimental results of Fig. 1 with theoretical predictions, we have obtained $d\epsilon_1/d\omega$ and $d\epsilon_2/d\omega$ by means of a Kramers-Kronig analysis. The results of this analysis are shown in Fig. 2(a) together with the corresponding spectra calculated from the $\mathbf{k}\cdot\mathbf{p}$ band structure[12] shown in Fig. 2(b). Also shown in Figs. 2(c) and 2(d) are the line shapes expected for M_1 critical points:

$$\frac{d\epsilon}{d\omega}=\frac{d\epsilon_1}{d\omega}+i\frac{d\epsilon_2}{d\omega}\sim i(\omega_g-\omega)^{-1/2}, \tag{1}$$

and for M_2 critical points:

$$\frac{d\epsilon}{d\omega}=\frac{d\epsilon_1}{d\omega}+i\frac{d\epsilon_2}{d\omega}\sim -(\omega_g-\omega)^{-1/2}. \tag{2}$$

It is apparent that the experimental line shapes differ considerably from those of the $\mathbf{k}\cdot\mathbf{p}$ calculation which correspond to M_1 critical points. The experimental spectrum has sharp negative peaks with an abrupt high-energy side for $d\epsilon_1/d\omega$, whereas from an M_1 edge $d\epsilon_1/d\omega$ should have an abrupt low-energy side. Similarly, the experimental $d\epsilon_2/d\omega$ is roughly symmetric about zero instead of the positive peaks shown in Figs. 2(b) and 2(c). Evidently, the experimental spectra are a mixture of the line shapes expected for M_1 critical points and M_2 critical points (see Fig. 2). The accidental degeneracy of M_1 and M_2 critical points at the energies of the E_1 and $E_1+\Delta_1$ peaks is excluded by our present theoretical knowledge of band structure of InSb.[12,13] Critical points in this energy range occur only in the Λ ($\langle 111\rangle$-type) directions and the reduced transverse masses for these

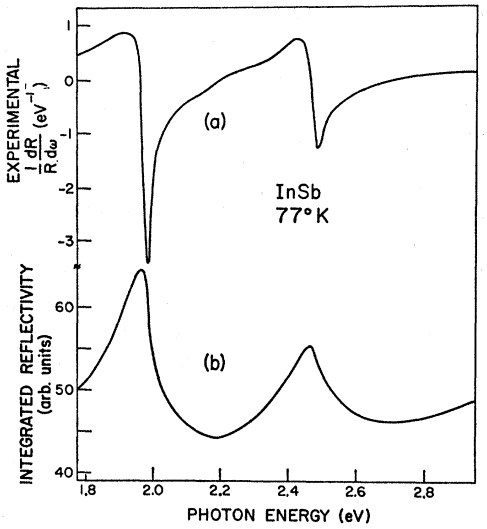

FIG. 1. (a) Logarithmic derivative of the reflectivity spectrum of InSb at 77°K in the neighborhood of the E_1 and $E_1+\Delta_1$ transitions. (b) Reflectivity spectrum of InSb obtained by numerically integrating the logarithmic derivative in (a).

directions are small and positive.[14] Hence, any critical points in the energy range of the $E_1-E_1+\Delta_1$ doublet must be either of the M_0 or of the M_1 variety. We must therefore examine the likelihood of exciton effects being responsible for the anomalous line shapes. One might already anticipated exciton effects because of the strong temperature dependence described above.

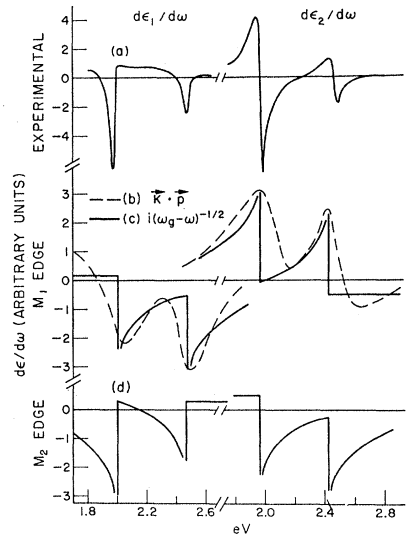

FIG. 2. (a) $d\epsilon_1/d\omega$ and $d\epsilon_2/d\omega$ for InSb obtained by Kramers-Kronig transform of Fig. 1(a). (b) $d\epsilon_1/d\omega$ and $d\epsilon_2/d\omega$ for InSb obtained by differentiating ϵ_1 and ϵ_2 from $\mathbf{k}\cdot\mathbf{p}$ band structure of Ref. 12. (c) Derivatives of the singular portions of ϵ_1 and ϵ_2 at an M_1 critical point. (d) Derivatives of the singular portions of ϵ_1 and ϵ_2 at an M_2 critical point.

[11] K. L. Shaklee, Ph.D. thesis, Brown University, 1968 (unpublished).

[12] C. W. Higginbotham, F. H. Pollak, and M. Cardona, in Proceedings of the International Conference on the Physics of Semiconductors, Moscow, 1968 (to be published).

[13] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

[14] Critical points along the threefold Λ axis have rotational symmetry about Λ. Hence, for an M_1 critical point the two positive masses are equal and in directions perpendicular to the Λ axis ($M_\perp$); the negative mass is along the symmetry axis ($M_\parallel$).

Since $|m_{\parallel}| \gg m_{\perp}$ for InSb,[15] the effect of the longitudinal motion of the electron with respect to the hole can be separated from the transverse motion in the spirit of the adiabatic approximation. However, modifications in either the effective-mass approximation or the Coulomb potential at $\mathbf{r}=0$ must be introduced in order to obtain resonance states (hyperbolic excitons) in the kind of approach at M_1 critical points.[3,4] Hence, it is more illuminating to discuss the experimental spectra of Fig. 2 on the basis of the theory of Toyozawa *et al.*[16] in which the exciton interaction causes the admixture of the M_1 and M_2 line shapes observed experimentally. These authors use a model electron-hole interaction extending only to nearest neighbors and show that the effect of a small attractive interaction at an M_j critical point is to mix M_j and M_{j+1} line shapes.[17] Thus, our experimental results can be easily explained on the basis of this simplified model of the exciton interaction.

There has been considerable controversy[7,18] as to the nature of the structure observed in the electroreflectance spectra of the E_1 and $E_1+\Delta_1$ transitions. While it is sometimes possible to explain these lines on the basis of the Franz-Keldysh effect associated with an M_1 critical point, it is interesting to note that a parallel explanation, which attributes the electroreflectance line shapes to a broadening of the exciton peaks by the modulating field, is also possible.[19]

[15] For the E_1 and $E_1+\Delta_1$ critical points of InSb $m_{\parallel} \simeq -10 m_{\perp}$.

[16] Y. Toyozawa, M. Inoue, T. Inoui, M. Okazaki, and E. Hanamura, Proc. Phys. Soc. Japan Suppl. **21**, 133 (1967).

[17] We take $M_4 = M_0$.

[18] B. O. Seraphin, Proc. Phys. Soc. (London) **87**, 235 (1966).

[19] Y. Hamakawa, P. Handler, and F. A. Germano, Phys. Rev. **167**, 709 (1968).

PHYSICAL REVIEW VOLUME 174, NUMBER 3 15 OCTOBER 1968

Decay Modes with Coherent Resonant-Energy Transfer between Deep Impurities in Solids*

R. C. CASELLA
National Bureau of Standards, Washington, D. C. 20234

(Received 10 June 1968)

Attention is called to the existence of new decay modes for deep impurities in solids associated with coherence in the resonant-energy transfer between them. The theoretical decay rate R of the two-impurity complex is of the form $R(t)=C_1\exp(-\gamma_1 t)+C_2\exp(-\gamma_2 t)+\exp[-\frac{1}{2}(\gamma_1+\gamma_2)t]\times \mathrm{Re}D\exp(-i\Delta t)$, with C_n, γ_n real positive, Δ real, and D complex. The oscillations in time t exhibited by the third term in the expression for R provide an experimental test for the coherence effect. The partial rate $R_r(t)$ for radiative decay is of the same form as the total rate $R(t)$. In the analysis, use is made of an analogy between the decay of the excited impurity complex and that of K^0 mesons in particle physics, where similar coherent oscillations have been observed experimentally.

I. INTRODUCTION

THE decay of excitation via resonant-energy transfer from an excited impurity of type A to a different species B is a well-known process in solids. The theory of this process has been treated extensively by Dexter,[1] who has also reviewed the earlier works of Kallmann and London,[2] Perrin,[3] and Förster.[4] The basic mechanism for the energy transfer involves virtual photon creation and annihilation (electric dipole-dipole and higher-multipole interactions in the near-zone electromagnetic field[5]), but other mechanisms involving virtual phonons, far-zone radiation photons, and other elementary excitations can contribute to the transfer process. Dexter[1] and others have treated the case of transfer between relatively broad overlapping impurity bands in crystals. For this case, one may consider the process to occur sequentially in several well-defined steps: (i) excitation of A, (ii) relaxation of A to a band overlapping in energy with an excitation band of B, (iii) transfer of the excitation from A to B, (iv) rapid relaxation of the excited B via strong lattice interactions until B is no longer in resonance with A, and (v) de-excitation of B with photon emission characteristic of B.

In the present paper,[6] we consider a somewhat

* Research supported by the National Bureau of Standards, U. S. Department of Commerce.

[1] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953). Contains references to earlier work, both experimental and theoretical. See, also, D. L. Dexter and R. S. Knox, *Excitons* (Interscience Publishers, Inc., New York, 1965), p. 24; and R. C. Powell, B. Di Bartolo, B. Birang, and C. S. Naiman, Phys. Rev. **155**, 296 (1967), which contain references to more recent work.

[2] H. Kallmann and F. London, Z. Physik. Chem. (Leipzig) **B2**, 207 (1929).

[3] J. Perrin, Compt. Rend. **184**, 1097 (1927).

[4] T. Förster, Ann. Physik **2**, 55 (1948).

[5] This process was invoked to explain energy transfer of excitons by W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).

[6] See also, R. C. Casella, Bull. Am. Phys. Soc. **13**, 439 (1968). One difference between the notation here and in Ref. 6 should be noted. M (here) $=2M$ (Ref. 6). That is, here M denotes twice the energy-shift matrix. [See Eq. (20) and the following comments.]