Resonant Light Scattering by Single-Particle Electronic Excitations in *n*-GaAs†

A. Pinczuk,* L. Brillson, and E. Burstein
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

and

E. Anastassakis
Department of Physics, Northeastern University, Boston, Massachusetts 02115

(Received 29 March 1971)

Resonant light scattering by single-particle excitations was observed in *n*-GaAs with incident photon energies near the $E_0+\Delta_0$ optical energy gap. We find that under extreme resonance conditions the spectra have two components with the scattered light polarization perpendicular and parallel to the incident light. These results are interpreted in terms of a random-phase-approximation theory.

We have observed resonant light scattering by single-particle electronic excitations (SPE) of *n*-GaAs in spectra excited with radiation having energies close to the optical $E_0+\Delta_0$ gap. This energy gap can be made almost equal to the energy of the laser photons by an appropriate choice of the electron concentration. The possibility of resonant Raman scattering from the electron gas of semiconductors via intermediate photon-induced interband transitions was first suggested by Wolff[1] and is implicit in the calculations of Hamilton and McWhorter[2] and Jha.[3] In the pioneering work on *n*-GaAs by Mooradian[4] the spectra were excited with photons having energies (1.17 eV) appreciably smaller than the E_0 gap (~1.51 eV). Resonant Raman scattering by SPE was observed in *n*-CdS by Scott and coworkers.[5] The results we present here were obtained under *extreme resonance* conditions for which $E(n)-\hbar\omega_1\approx\hbar qv_F$, where $E(n)$ is the $E_0+\Delta_0$ gap at electron concentration n, ω_1 is the frequency of the incident photons, q is the scattering wave vector, and v_F is the Fermi velocity of the electrons.

The low-temperature spectra of SPE have two polarization components: *component I,* in which the scattered light has polarization perpendicular to the incident light; and *component II,* in which the scattered light has polarization parallel to the incident light. Component I was observed by Mooradian[4] in *n*-GaAs and has been assigned to spin-density fluctuations of the electron gas. Component II is very weak in Mooradian's low-temperature spectra because the SPE that originate this component are charge-density fluctuations which, for the wave vectors involved in light-scattering experiments, are screened by electron-electron interactions. Component II appears in the higher-temperature spectra and has been accounted for by the temperature dependence of resonant denominators.[6] Component II was absent in the low-temperature spectra of *n*-CdS.[7]

In our low-temperature spectra obtained under extreme resonance conditions we found components I and II with about the same intensity. This result indicates that under these conditions, the SPE contributing to component II are no longer equivalent to pure charge-density fluctuations but have a more complex character and therefore are not completely screened by the Coulomb interactions of the electron gas.

Spectra were obtained from (110) cleavage surfaces using a back-scattering geometry, and the samples were cooled in a low-temperature Dewar by a stream of cold He gas. Two excitation sources were used: the 6328-Å (1.96-eV) emission from a He-Ne laser and the 6471-Å (1.92-eV) emission from a Kr^+ laser. In order to reduce its power density, the incident radiation was focused into the sample surface with a cylindrical lens. The penetration depth of this radiation inside the crystals is ~3000 Å,[8] much larger than the width of their surface space-charge regions. The $E_0+\Delta_0$ energy gap is located, at low temperatures, between 1.85[9] and 1.88 eV.[10] Samples for which we have obtained good spectra have Fermi energies ranging from 0.02 to 0.14 eV. Therefore, the carrier-density-dependent optical $E_0+\Delta_0$ gap of the samples can be adjusted between ~1.87 and ~2.0 eV to match closely the energy of the incident photons.

Figure 1 shows spectra obtained from a GaAs sample with $n=1.3\times10^{18}$ cm^{-3} using the 6471-Å

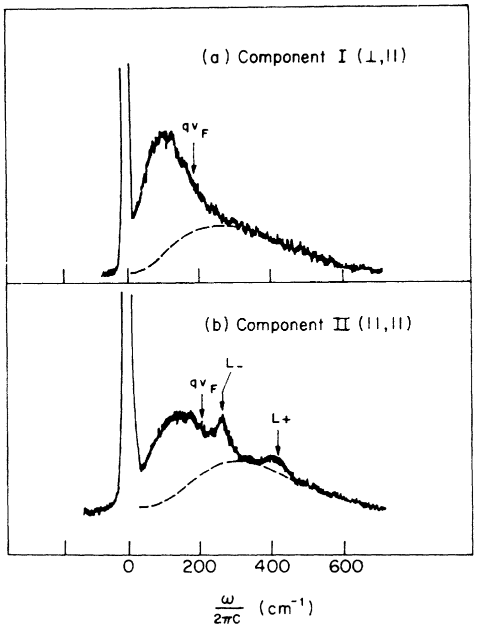

FIG. 1. Light scattering spectra of SPE and coupled longitudinal phonon-plasmon modes (at L_- and L_+) in GaAs for $n = 1.3\times10^{18}$ cm^{-3} at 10°K. The dashed line represents the estimated luminescence background.

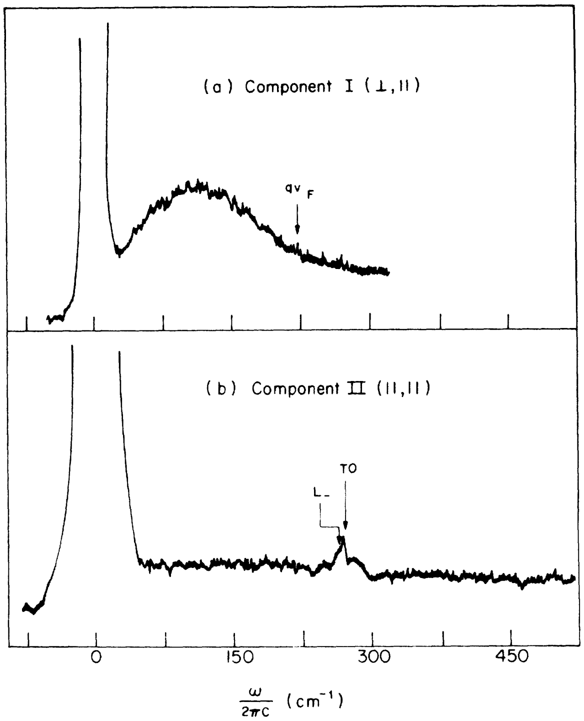

FIG. 2. Light scattering spectra of GaAs for $n = 2.03\times10^{18}$ cm^{-3} at 10°K.

(1.92-eV) line. The spectra show components I and II with about the same intensity. That these spectra are due to SPE is demonstrated by the cutoff (smeared by collision broadening) near qv_F. The values of qv_F for our experiments are larger than those in Mooradian's because our scattering wave vector ($q \simeq 7\times10^5$ cm^{-1}) is about three times larger. As a consequence, the wave vector dependence of the plasma frequency had to be considered to explain the observed values of the frequencies of the coupled longitudinal phonon-plasmon modes.[8] In Fig. 1(b) these modes appear at $\omega_- = 265$ cm^{-1} and $\omega_+ \simeq 420$ cm^{-1}. Figure 2 shows the spectra obtained from a sample with $n = 2.03\times10^{18}$ cm^{-3} using the same excitation. The spectra show only component I of the SPE, and Fig. 2(b) shows $\omega_- \simeq 270$ cm^{-1} while ω_+ is absent. The luminescence backgrounds in Figs. 1 and 2 are completely different. The luminescence background[11] in Fig. 1 is due mainly to the $E_0 + \Delta_0$ gap. This luminescence is not excited in the spectra of Fig. 2 because the gap at $n = 2.03\times10^{18}$ cm^{-3} is larger than the energy of the laser photons. The shape of the luminescence in Fig. 1 was estimated from the spectra obtained from a sample with $n = 3.55\times10^{17}$ cm^{-3}. In the spectra of Figs. 1 and 2 the intensities of the scattered light and the luminescence are weak. This is due to the small skin depth which is determined mainly by transitions from highest-energy valence bands to the conduction band.

We have also obtained spectra from samples having $n = 3.55\times10^{17}$ cm^{-3} and 5.1×10^{17} cm^{-3} with the 6471-Å (1.92-eV) excitation; in all cases the SPE spectra are much weaker than those obtained from the $n = 1.3\times10^{18}$ cm^{-3} sample. The intensity of component I in the spectrum of Fig. 2(a) is about an order of magnitude smaller than that of Fig. 1(a). The SPE are absent in spectra obtained from these samples with the 6328-Å (1.96-eV) excitation. However, with this excitation we obtained strong spectra from a sample with $n = 4.8\times10^{18}$ cm^{-3} for which extreme resonance conditions exist again. Of all the samples that we have studied with a 6471-Å (1.92-eV) excitation, the sample with $n = 1.3\times10^{18}$ cm^{-3} is the one which has the largest resonance enhancement.

The most interesting result from the point of view of the microscopic mechanisms which are responsible for the scattering of light, as shown by Figs. 1 and 2, is that the intensity of component II is more dependent on the resonant enhancement than the intensity of component I. In fact, the appearance of component II in the low-temperature spectra is a direct consequence of extreme resonance conditions. The cross section for light scattering by the electron gas within the random-phase approximation (RPA) is given by[2,3]

$$\frac{d^2\sigma}{d\Theta d\Omega}=r_0{}^2\,\frac{\omega_2}{\omega_1}\,\frac{1}{1-e^{-\beta\hbar\Omega}}\left(\frac{-\hbar}{\pi}\right)\mathrm{Im}\sum_k M(\vec{k},\vec{q},\Omega)\,|\langle\vec{k}+\vec{q}|t_{21}|\vec{k}\rangle_{\mathrm{RPA}}|^2, \tag{1}$$

where ω_1 and ω_2 are the incident and scattered frequencies, $\Omega=\omega_1-\omega_2$, r_0 is the classical radius of the electron, and

$$M(\vec{k},\vec{q},\Omega)=\frac{f(\vec{k}+\vec{q})-f(\vec{k})}{e(\vec{k}+\vec{q})-e(\vec{k})-\hbar\Omega}; \tag{2}$$

the $e(\vec{k})$ are one-electron energies in the conduction band at wave vector $\vec{k}$ and $f(\vec{k})$ is the Fermi distribution function at $e(\vec{k})$. The dielectric constant of the electron gas is given by

$$\epsilon(\vec{q},\Omega)=1-(4\pi e^2/q^2)\sum\nolimits_k M(\vec{k},\vec{q},\Omega). \tag{3}$$

For component II of the spectra, at resonance we have the following expression for the scattering amplitude:

$$\langle\vec{k}+\vec{q}|t_{21}|\vec{k}\rangle_{\mathrm{RPA}}=\frac{\langle c|\vec{p}\cdot\hat{e}_1|v\rangle\langle v|\vec{p}\cdot\hat{e}_2|c\rangle}{m}\left\{\frac{1}{E(\vec{k}+\vec{q})-\hbar\omega_1}+\frac{2\pi e^2}{q^2\epsilon(\vec{q},\Omega)}\left[\sum_{k'}\frac{M(\vec{k}',\vec{q},\Omega)}{E(\vec{k}')-\hbar\omega_1}+\sum_{k'}\frac{M(\vec{k}',\vec{q},\Omega)}{E(\vec{k}')-\hbar\omega_2}\right]\right\}, \tag{4}$$

where $\hat{e}_1$ and $\hat{e}_2$ are unit polarization vectors of the incident and scattered light, $\langle c|\vec{p}|v\rangle$ is the interband matrix element of electron momentum, and $E(\vec{k})$ is the energy gap at wave vector $\vec{k}$. The possible values of $\vec{k}$ are restricted by the conservation of wave vector and the Pauli principle. The second and third terms in Eq. (4) are due to the Coulomb interaction between the electrons and are absent in the scattering amplitude for component I of the spectra.

Under nonresonant conditions, $E(\vec{k})-\hbar\omega_1\simeq E(\vec{k})-\hbar\omega_2\gg\hbar\Omega$ and $\langle\vec{k}+\vec{q}|t_{21}|\vec{k}\rangle_{\mathrm{RPA}}$ are independent of $\vec{k}$. Under such conditions, the SPE making a contribution to component II of the spectra can be considered as charge-density fluctuations. The screening effects of the electron gas are predicted by Eq. (4) because the first term is almost canceled by the other two. As resonance is approached, the $\vec{k}$ and $\vec{k}'$ dependence in the denominators of Eq. (4) cannot be neglected and a cancelation no longer occurs. The SPE which are excited under these conditions are not equivalent to pure charge-density fluctuations. The dependence of these effects on resonance conditions can be studied by expanding the resonant denominators in series of the type

$$\frac{1}{E(\vec{k}')-\hbar\omega_1}\simeq\frac{1}{E(\vec{k}+\vec{q})-\hbar\omega_1}+\frac{E(\vec{k}+\vec{q})-E(\vec{k}')}{[E(\vec{k}+\vec{q})-\hbar\omega_1]^2}+\cdots, \tag{5}$$

$$\frac{1}{E(\vec{k}')-\hbar\omega_2}\simeq\frac{1}{E(\vec{k}+\vec{q})-\hbar\omega_1}+\frac{\hbar\Omega}{[E(\vec{k}+\vec{q})-\hbar\omega_1]^2}+\frac{E(\vec{k}+\vec{q})-E(\vec{k}')}{[E(\vec{k}+\vec{q})-\hbar\omega_1]^2}+\cdots. \tag{6}$$

When expansions of this type are inserted in Eq. (4), the terms which will give a contribution not screened by the dielectric constant of the electron gas will be proportional to powers of the resonant denominators which are larger than 1.

The scattering amplitude of component I is proportional to the first power of the resonant denominators. Therefore, on the basis of Eqs. (4), (5), and (6) a stronger dependence on resonance conditions is predicted for component II. This is in agreement with the results shown in Figs. 1 and 2. Equations (5) and (6) show that component II will have an intensity comparable to that of component I when $E(\vec{k}+\vec{q})-\hbar\omega_1\approx E(\vec{k}+\vec{q})-E(\vec{k}')$ and $E(\vec{k}+\vec{q})-\hbar\omega_1\approx\hbar\Omega$. The conditions define the regime of extreme resonance as that for which $E(n)-\hbar\omega_1\approx\hbar qv_{\mathrm{F}}$.

Under extreme resonance conditions, expansions like those of Eqs. (5) and (6) are expected to give only qualitative descriptions, and in addition there may be contributions from real interband electronic transitions. Therefore, it would be desirable to have a more rigorous theory of resonant light scattering by SPE.

---

†Work supported by the Advanced Research Projects

Agency and the U. S. Army Research Office (Durham).

*Present address: Comisión Nacional de Energía Atómica, Avda. del Libertador 8250, Buenos Aires, Argentina.

[1] P. A. Wolff, Phys. Rev. Lett. 16, 225 (1966).

[2] D. C. Hamilton and A. L. McWhorter, in *Light Scattering Spectra of Solids,* edited by G. B. Wright (Springer, Berlin, 1969), p. 309.

[3] S. S. Jha, Nuovo Cimento 63B, 331 (1969).

[4] A. Mooradian and A. L. McWhorter, in *Light Scattering Spectra of Solids,* edited by G. B. Wright (Springer, Berlin, 1969), p. 297.

[5] J. F. Scott, T. C. Damen, R. C. C. Leite, and J. Shah, Phys. Rev. B 1, 4330 (1970).

[6] A. L. McWhorter, A. Mooradian, and D. C. Hamilton, to be published.

[7] J. F. Scott, T. C. Damen, J. Ruvalds, and A. Zawadowski, Phys. Rev. B 3, 1295 (1971).

[8] M. D. Sturge, Phys. Rev. 127, 768 (1962).

[9] A. Pinczuk, L. Brillson, E. Burstein, and E. Anastassakis, to be published.

[10] D. D. Sell and S. E. Stokowski, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass., 1970,* edited by S. P. Keller, J. C. Hensel, and F. Stern, CONF-700801 (U. S. AEC Division of Technical Information, Springfield, Va., 1970), p. 417.

[11] A. Mooradian [Phys. Rev. Lett. 22, 185 (1969)] has looked for SPE scattering in Cu-Au alloys but only observed photoluminescence.

Anharmonicity and the Temperature Dependence of the Forbidden (222) Reflection in Silicon*

David Keating and Anthony Nunes
Brookhaven National Laboratory, Upton, New York 11973

and

Boris Batterman and Jerome Hastings
Department of Material Science and Engineering, Cornell University, Ithaca, New York 14850

(Received 14 May 1971)

We have measured the "forbidden" (222) reflection of neutrons from silicon between 15 and 1353°C. We have used these measurements to correct the x-ray (222) structure factor for the anharmonic motion of the atoms. The scattering from the anticentrosymmetric valence charge density obtained in this way is found to be less temperature dependent than that from the core. We take this as evidence of the failure of the rigid-ion model.

We report in this Letter success in detection of the "forbidden" neutron (222) reflection and measurement of its absolute intensity from room temperature to 1350°C. We present the results of these measurements and the conclusion to be drawn from them. A more detailed description of the experiment will appear elsewhere.[1]

The (222) structure factor (as well as any reflection for which $h+k+l=4n+2$, where n is an integer) would be identically zero if two silicon atoms in the unit cell had a centrosymmetric distribution of scattering matter. The two silicon atoms lie on two fcc lattices (denoted A and B) separated by $\frac{1}{4}$ of the cube diagonal. The sites of these two lattices both have T_d point symmetry, but the sites on B differ from those on A by inversion symmetry. For quadricovalent silicon, tetrahedral orientation of bonds is expected with $3s$-$3p$ hybridization.[2] The tetrahedral hybrid from the A site is able to overlap strongly with the oppositely directed hybrid of the B site, giving strong bonding and a net charge density that is anticentrosymmetric with respect to either site. This has long been recognized as the explanation for the otherwise forbidden reflections observed in diamond structures.[3] A recent x-ray measurement[4] gives $F(2,2,2)=1.46\pm0.04$ for silicon.

However, another possible cause for site asymmetry can exist in diamond structures. Because of its tetrahedral environment, each atom sees a nearest neighbor in one direction and a "hole" in the opposite direction. At high temperatures, we might anticipate that an atom spends more of its time making excursions toward the hole than toward its neighbor. This anharmonicity in atomic motions would create a time-averaged asymmetry, also tetrahedral, in the nuclear distribution. When considered together, anharmonic motion of the core charge and distribution of bonding