PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Evidence for a Dielectric Singularity in HgSe and HgTe†

J. G. Broerman

McDonnell Research Laboratories, McDonnell Douglas Corporation, St. Louis, Missouri 63166

(Received 6 April 1970)

New experimental data on the low-temperature mobility of n-type HgSe in the concentration range 2×10^{17}–5×10^{18} cm^{-3} are compared with a random-phase-approximation (RPA) calculation and a concentration-independent dielectric-constant calculation. The effects of band nonparabolicity and the p-like nature of the conduction-band wave function on the scattering calculation are included. The RPA calculation is in excellent agreement with the data, while the results of the concentration-independent dielectric-constant calculation are much too low. New experimental data on HgTe in the concentration range 1.6×10^{15}– 4×10^{18} cm^{-3} are also examined. At 1.6×10^{15} cm^{-3}, the RPA calculation agrees exactly with experiment, while the concentration-independent dielectric-constant calculation is too low by a factor of 3. In contrast to the case of grey tin, these results strongly support the RPA and hence the dielectric singularity predicted for symmetry-induced zero-gap semiconductors.

Semimetals with a small or vanishing overlap of valence-band maximum and conduction-band minimum have recently attracted considerable interest as sites for an excitonic phase transition.[1] One class of such materials, an example of which is grey tin (α-Sn),[2] is characterized by a symmetry-induced degeneracy of the band edges. If one ignores overlaps of the order of 10^{-4}–10^{-3} eV produced by small antisymmetric spin-orbit terms in the single electron Hamiltonian, then the zinc-blende analogs of α-Sn, HgSe, and HgTe also belong in this class.

However, it has been shown that the random-phase-approximation[3] (RPA) dielectric function $\epsilon(q)$ for intrinsic materials of this kind diverges at zero momentum transfer.[4] The presence of impurity carriers removes the singularity leaving a finite interband part $\epsilon_I(q)$ which is strongly dependent on carrier concentration.[5] This strong concentration dependence of the dielectric function should produce a striking anomaly in the concentration dependence of the low-temperature mobility.[5-7]

Several investigations[5–7] of the low-temperature mobility of degenerate n-type α-Sn have been carried out. The experimental values[8,9] are obtained from samples believed to be antimony doped. Thus, the limiting scattering mechanism for electrical conduction should be scattering by singly ionized impurities. The mobilities calculated[7] using the RPA dielectric function and singly ionized scatterers are larger than the experimental values by a factor of ≈ 3 at low concentrations. On the other hand, the mobilities calculated[6] using the concentration-independent background dielectric constant ϵ_0 are in excellent agreement with experiment. However, doubly ionized donors cannot be ruled out, and the RPA calculation[7] gives reasonably good agreement with experiment for doubly ionized scatterers. Thus, the picture with regard to α-Sn remains unclear until more is known about the charge states of the impurities.

The original investigation[10] of the low-temperature mobility of HgSe was directed toward a determination of the band structure, and it was shown that mobilities calculated for Γ_8 electrons with a concentration-independent dielectric constant were in good agreement with Whitsett's[11] experimental values. However, two points which lie so far above typical values that Whitsett felt them to be in error remained unexplained. Since that time more accurate band parameters have become available[12] and a number of other anomalously high mobilities have been reported both in our laboratory[13] and in the literature.[12] For these reasons, and because of the situation with regard to α-Sn, it was felt worthwhile to reexamine HgSe.

The conduction-valence–band overlap in this structure arises from antisymmetric spin-orbit couplings to higher-lying Γ_{15} and Γ_{12} levels which produce linear terms in the valence-band dispersion relation at the zone center. One can estimate the overlap to be in the neighborhood of 10^{-3} eV, and this is supported by an analysis of Hall data.[14] This energy is about $\frac{1}{50}$ of the Fermi energy of the lowest-concentration sample considered here, and thus will be ignored in the dielectric-function calculation. With this approximation, the results of Ref. 7 are applicable. The ionized-impurity-limited conductivity in the RPA is given by[7]

$$\sigma=\frac{6\pi}{\hbar}\left(\frac{\hbar^2}{2\mu m_0}\right)^3\frac{\epsilon_I^2(0)}{e^2E_g}\frac{n_e}{Z_i}\frac{k_F^2}{\lambda^2(\xi_F)\Phi(k_F)}\quad, \tag{1}$$

where

$$\Phi=\int_{-1}^{1}\frac{(1-x)}{(Ax^2+Bx+C)^2}\,\frac{1}{2}\sum_{\mu\mu'}\left|\int_{\text{cell}}\chi_{k\mu}^*\,\chi_{k'\mu'}\,d^3r\right|^2dx\quad, \tag{2}$$

$$A=-2(k/k_F)^2[1-\epsilon_0/\epsilon_I(0)]a' \ , \quad (3)$$

$$B=-1+4(k/k_F)^2[1-\epsilon_0/\epsilon_I(0)]a' \ , \quad (4)$$

$$C=(1/2k^2)\{k_{\mathrm{FT}}^2/\epsilon_I(0) + 2k^2[1-2(k/k_F)^2[1-\epsilon_0/\epsilon_I(0)]a']\} \ . \quad (5)$$

Here μ is the zone center cyclotron mass ratio, n_e is the electron concentration, Z_i is the charge of the donor, E_g is the $\Gamma_8-\Gamma_6$ splitting, x is the cosine of the angle between k and k', k_F is the Fermi momentum, k_{FT} is the Fermi-Thomas momentum, $\xi_F=E_F/E_g$ with E_F the Fermi energy, $\epsilon_I(0)$ is the interband part of the dielectric function at zero momentum transfer, a' is a constant $\approx\frac{1}{12}$, $\chi_{k\mu}$ is the cell-periodic part of the conduction-band wave function, and λ is a function proportional to the density of states.[6] One can further show

$$\frac{1}{2}\sum_{\mu\mu'}\left|\int_{\mathrm{cell}}\chi_{k\mu}^*\chi_{k'\mu'}\,d^3r\right|^2=\sum_{i=0}^{2}\pi_i x^i \ , \quad (6)$$

where π_i are defined in Ref. 6. In deriving this result, we have used the expression for $4\pi\alpha^{\mathrm{INTER}}$ given in Ref. 5, which can be shown numerically to be accurate to about 7% for the nonparabolic conduction band of HgSe. This yields a maximum error of about 0.2% in $\epsilon_I(q)$. These results also take into account the effects of band nonparabolicity and p-like character of the wave function on the scattering calculation. Using Eq. (6), an analytical expression can be found[7] for the scattering function Φ. The results are rather lengthy and will not be given here. The Fermi energy is found by a solution of Kane's[15] three-band secular equation.

In the evaluation of σ, we use the band parameters determined by Galazka, Seiler, and Becker.[12] They find $P=7.2\times10^{-8}$ eV cm, $E_g=0.22$ eV, and $\Delta=0.45$ eV (P is Kane's $\langle\Gamma_1|\vec{p}|\Gamma_{15}\rangle$ matrix element and Δ is the Γ_{15} spin-orbit splitting). The result of this calculation for singly ionized impurities is the solid curve of Fig. 1. The dashed curve is the result of a calculation like that of Ref. 6 with a concentration-independent background dielectric constant. The dotted curve is the mobility of a band with the same shape as HgSe but with Γ_6 band-edge symmetry. The experimental points[11-13] are believed to be accurate[16] to 5% in Hall concentration and 10% in mobility. The sample denoted by a cross has been doped with 10^{19}-cm^{-3} sulfur, and all other samples are "pure" HgSe. As can be seen, the highest mobility samples in every concentration range are in good agreement with the RPA calculation but lie much higher than the concentration-independent dielectric-constant curve.

Unfortunately, good samples of HgSe with electron concentrations below 10^{17} cm^{-3} have not been obtained. The material problem in HgTe is just the opposite of this: Crystals grow naturally with large numbers of acceptors, probably doubly ionized Hg vacancies, and it is very difficult to produce good n-type samples. Recently, Ivanov-Omskii *et al.*[17] have been able to reduce the acceptor concentrations by annealing in Hg vapor and obtain n-type samples with the highest mobilities so far reported.

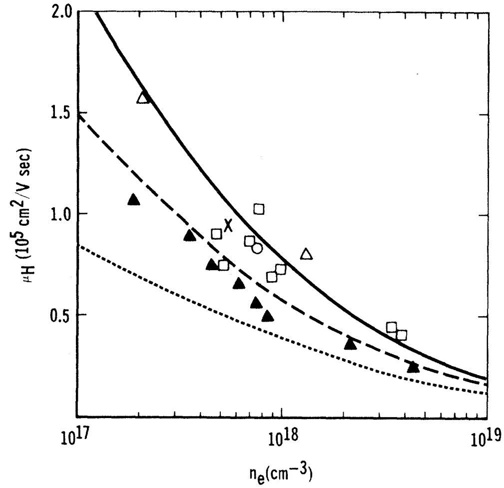

FIG. 1. Ionized-impurity-limited Hall mobility of HgSe. The solid curve is for the RPA dielectric function, dashed curve for a concentration-independent dielectric constant, dotted curve for a band with the same shape but Γ_6 band-edge symmetry. Triangles are from Ref. 11, squares from Ref. 12, and the cross and circle from Ref. 13.

In the calculation of the mobility of HgTe, we use the values of P and E_g obtained by Pidgeon and Groves.[18] Cardona *et al.*[19] report the $\Lambda_3-\Lambda_1$ splitting and we use the two-thirds rule to obtain $\Delta=1$ eV. For the background dielectric constant we use the value obtained by Dickey and Mavroides.[20] The overlap is not known but is probably considerably less than that of HgSe since the antisymmetric spin-orbit couplings should be much smaller.

The results of this calculation for singly ionized donors are displayed in Fig. 2. The solid family of curves represent the RPA calculation for different concentrations of doubly ionized acceptors. The dashed curve is the concentration-independent dielectric-constant calculation. The experimental points are some of the higher mobility samples of Ref. 17. The lowest-concentration sample lies at 1.6×10^{15} cm^{-3} and has a Hall mobility of 0.95×10^6 cm^2/V sec. This value is in exact agreement with the RPA calculation and is larger than the concentration-independent dielectric-constant calculation by a factor of ≈3. As one moves to higher concentrations, the data fall increasingly below the donors-only curves, presumably due to partial

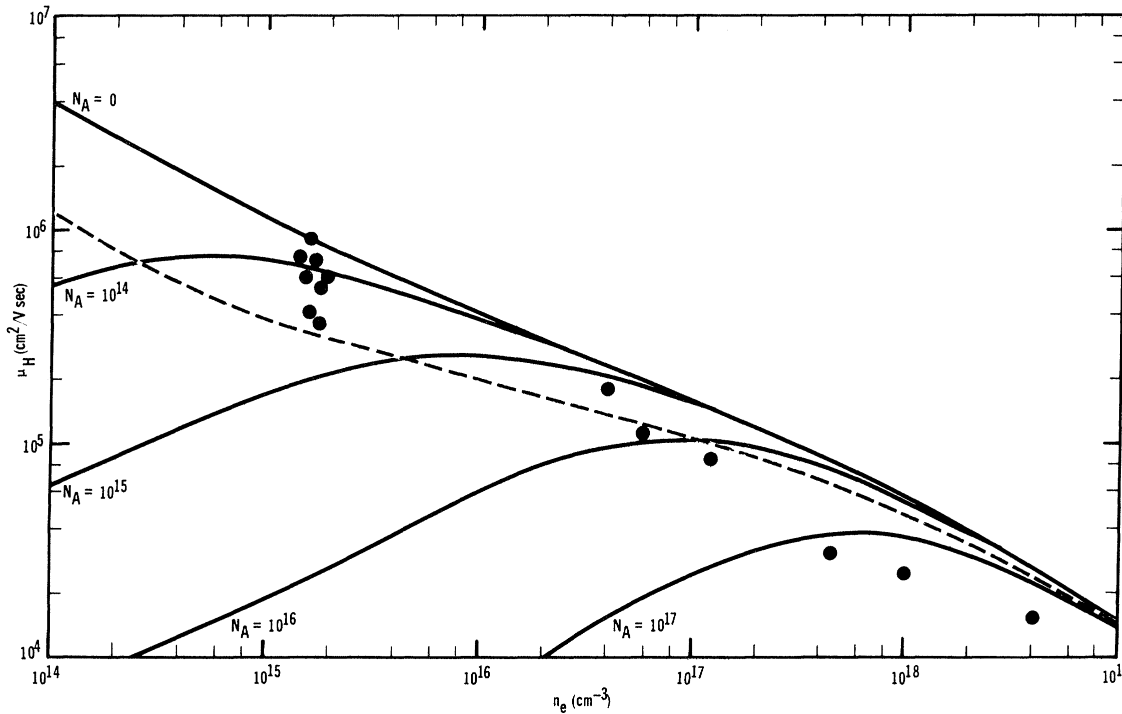

FIG. 2. Ionized-impurity-limited Hall mobility of HgTe for a variety of concentrations of doubly ionized acceptors (solid curves). The dashed curve is the concentration-independent dielectric-constant calculation. The experimental data are from Ref. 17.

compensation by doubly ionized acceptors.

The enhancement of the mobility of the 1.6×10^{15}-cm^{-3} sample over the background dielectric-constant mobility by a factor of 3 clearly indicates a large enhancement of ϵ_I. However, the exact agreement with the RPA calculation may be fortuitous because of our uncertainty about the magnitude of the overlap. The Fermi energy at this concentration is about 0.002 eV. If the overlap is of the order of 10^{-4} eV, then the result is practically exact. However, if the overlap is of the order of 10^{-3} eV, ϵ_I would be enhanced considerably more than our calculation indicates, and the observed mobility could be accounted for by partial compensation. A calculation including the effect of the overlap, even if it were known, would be extremely difficult because of the complicated shape of the valence band near the zone center. More data on uncompensated samples in the 10^{16}-cm^{-3} range, where the overlap is less important, would be very useful, as would a firm value for the overlap.

Thus, we conclude that although the situation is at present ambiguous for α-Sn, the data strongly support the RPA, and hence the dielectric singularity, in HgSe. The data for HgTe clearly indicate a large enhancement of the dielectric constant, but it is not possible at this time to say with certainty that the enhancement agrees with that predicted by the RPA.

I would like to thank Dr. R. R. Galazka, Dr. D. G. Seiler, and Dr. W. M. Becker for communicating their work to me prior to publication, Dr. S. L. Lehoczky and D. A. Nelson for the use of their mobility data, Dr. C. R. Whitsett for useful discussions of this problem, and Dr. D. P. Ames for support of this work. I am grateful to Dr. V. K. Ogorodnikov for bringing Ref. 17 to my attention, and to Dr. Ram Levy for assistance in translation from the Russian.

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†Research conducted under the McDonnell Douglas Independent Research and Development Program.

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PHYSICAL REVIEW B VOLUME 2, NUMBER 6 15 SEPTEMBER 1970

Wave-Vector-Dependent Dielectric Function for Si, Ge, GaAs, and ZnSe†

John P. Walter* and Marvin L. Cohen‡
Department of Physics, University of California, Berkeley, California 94720
(Received 11 May 1970)

The longitudinal wave-vector-dependent dielectric function $\epsilon(\vec{q})$ is calculated for Si, Ge, GaAs, and ZnSe. The energy eigenvalues and wave functions which are used have been obtained from energy-band calculations based on the empirical pseudopotential method. Explicit results are given in the [1,0,0], [1,1,0], and [1,1,1] directions in the range $0 \leq q \leq (4\pi/a)$. A comparison is made between the present results and the results of other calculations. Some comparisons with experiment are also made.

I. INTRODUCTION

In this paper we present a calculation of the static longitudinal wave-vector-dependent dielectric function $\epsilon(\vec{q})$ for the cubic semiconductors Si, Ge, GaAs, and ZnSe. $\epsilon(\vec{q})$ describes the response of a crystal to an electric field parallel to $\vec{q}$:

$$\vec{D}e^{i\vec{q}\cdot\vec{r}} = \epsilon(\vec{q})\vec{E}e^{i\vec{q}\cdot\vec{r}} . \tag{1.1}$$

For most applications we are interested in either static fields or fields varying with phonon frequencies; in this frequency region we may replace the frequency-dependent dielectric function with the static dielectric function $\epsilon(\vec{q})$, an approximation which is accurate to within 0.1%.

Using the expression for $\epsilon(\vec{q})$ given by Ehrenreich and Cohen,[1] we obtain

$$\epsilon(\vec{q}) = 1 + \frac{8\pi e^2}{q^2} \sum_{\vec{k},c,v} \frac{|\langle \vec{k}+\vec{q}, v | \vec{k}, c\rangle|^2}{E_c(\vec{k}) - E_v(\vec{k}+\vec{q})} , \tag{1.2}$$

where $\vec{k}$ is summed over the first Brillouin zone, v over the valence bands, and c over the conduction bands. In our calculations we use electronic wave functions and energy eigenvalues which have been calculated using the empirical pseudopotential method.[2] Spin-orbit effects have not been included.

Calculations of $\epsilon(\vec{q})$ for semiconductors were first performed by Penn,[3] using a model isotropic semiconductor. These calculations have recently been redone by Srinivasan.[4] The present calculations agree fairly well with Srinivasan's calculations except that our results exhibit a slight anisotropy. Calculations based on more realistic band models for Si and Ge have been performed by Nara.[5] Despite the fact that his model is almost identical to ours, his results disagree to some extent with our results. In particular, he finds a strong anisotropy in $\epsilon(\vec{q})$ at small q which is missing from our results. In addition, our calculations show $\epsilon(\vec{q})$ to be a monotonically decreasing function of $|\vec{q}|$, a feature which is not present in the results of Srinivasan or of Nara (see Fig. 1).

$\epsilon(\vec{q})$ has had many applications; it has been used to calculate the lattice vibration spectrum of sili-