Ionized-Impurity-Limited Mobility and the Band Structure of Mercuric Selenide*

J. G. BROERMAN
McDonnell Research Laboratories, McDonnell Douglas Corporation, St. Louis, Missouri 63166
(Received 11 February 1969)

A calculation is performed, in the Born approximation, of the ionized-impurity-limited conductivity of a conduction band with the Kane form, taking into account the symmetry of the conduction-band wave functions. Using the band parameters for mercuric selenide obtained by Whitsett from Shubnikov–de Haas measurements, it is shown that Whitsett's 4.2 K mobilities as a function of electron concentration are in excellent agreement with the results of a calculation for a Γ_8 band edge, but not with those for a Γ_6 band edge. It is also pointed out that Whitsett's band parameters require a much smaller valence-band overlap than that obtained by Harman. These results indicate an inverted, gray-tin-type structure for mercuric selenide.

1. INTRODUCTION

IT is known that mercuric selenide is a II-VI compound which crystallizes in the cubic zinc-blende structure. A large number of its electrical and optical properties have been studied,[1–8] and it is generally believed that it is a semimetal or degenerate semiconductor, with a nearly spherical,[1] highly nonparabolic[1,6] conduction band, overlapped by a high-mass valence band.[5]

Whitsett's[1] experiment is especially interesting from the point of view of the band structure of HgSe. He measured the oscillatory magnetoresistance in samples whose conduction-electron densities ranged from 2×10^{17} to 4.5×10^{18} electrons/cm^3. From an analysis of the temperature dependence of the Shubnikov–de Haas oscillations, he was able to determine the cyclotron effective mass at the Fermi surface as a function of electron concentration. He then showed that these effective masses were consistent with a model similar to the Kane[9] model for the conduction band of InSb, and obtained the band parameters. In this model, the conduction-band minimum lies at the zone center and may have either Γ_6 (conventional germanium structure) or Γ_8 symmetry (inverted, gray-tin structure[10]). Roth *et al.*[11] subsequently analyzed the beat frequencies of the Shubnikov–de Haas oscillations, and showed that they were consistent with beats which would be produced by the inversion asymmetry splittings present in these band types.

With this in mind, a calculation of the low-temperature mobility as a function of electron concentration now becomes interesting for two reasons. First, the mobility depends on the effective mass at the Fermi surface and a calculation of its dependence on concentration, using Whitsett's band parameters, would provide independent confirmation of his model for the band structure. Second, as we will show, such a calculation can, in principle, distinguish the symmetry type of the conduction band. This arises because the scattering probability for p-like electrons (Γ_8 symmetry) has an angular dependence different from that for s-like electrons (Γ_6 symmetry). We will show that Whitsett's low-temperature mobilities are quite accurately predicted by ionized impurity scattering of conduction electrons whose zone-center symmetry type is Γ_8.

2. CONDUCTION-BAND STRUCTURE

We assume a conduction-band dispersion relation of the form

$$E=\frac{\hbar^2k^2}{2m_0}-\frac{E_g}{2}+\frac{1}{2}\left(E_g^2+\frac{8}{3}P^2k^2\right)^{1/2}. \quad (1)$$

This is Kane's[9] result for the case of the Γ_{15} spin-orbit splitting much larger than the $|\Gamma_8\text{-}\Gamma_6|$ difference, E_g. P is the momentum matrix element defined by Kane. If Cardona and Harbeke's[7] assignment of the structure in the spectrum of HgSe around 3 eV to a $\Lambda_3\text{-}\Lambda_1$ transition is correct, then application of the $\frac{2}{3}$ rule yields a Γ_{15} spin-orbit splitting of about 0.5 eV. If the conduction-band edge is Γ_6, then this dispersion relation ignores the coupling to the Γ_7 level (split-off valence band) which would lie about three times the $\Gamma_6\text{-}\Gamma_8$ energy difference from the Γ_6 level. Further, the $\Gamma_6\text{-}\Gamma_7$ coupling is less than the $\Gamma_6\text{-}\Gamma_8$ coupling by a factor of $2^{-1/2}$. Thus, one would expect this dispersion relation to be fairly accurate for energies less than E_g. If the conduction band is Γ_8, then the approximation should be very good since Γ_8 is not coupled to Γ_7 in first order. In either case it should be noted that Whitsett's values of the band parameters are obtained by fitting his experimental effective masses to this dispersion relation. If

* Research conducted under the McDonnell Douglas Independent Research and Development Program.
[1] C. R. Whitsett, Phys. Rev. **138**, A829 (1965). This paper provides an excellent review of work on HgSe.
[2] D. Redfield, Bull. Am. Phys. Soc. **2**, 121 (1957).
[3] C. R. Whitsett, J. Appl. Phys. **32**, 2257 (1961).
[4] H. Gobrecht, U. Gerhardt, B. Peinemann, and A. Tausend, J. Appl. Phys. **32**, 2246 (1961).
[5] T. C. Harman and A. J. Strauss, J. Appl. Phys. **32**, 2265 (1961).
[6] G. B. Wright, A. J. Strauss, and T. C. Harman, Phys. Rev. **125**, 1534 (1962).
[7] M. Cardona and G. Harbeke, J. Appl. Phys. **34**, 813 (1963).
[8] T. C. Harman, J. Phys. Chem. Solids **25**, 931 (1964).
[9] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).
[10] S. Groves and W. Paul, Phys. Rev. Letters **11**, 194 (1963).
[11] L. M. Roth, S. H. Groves, and P. W. Wyatt, Phys. Rev. Letters **19**, 576 (1967).

one calculates the cyclotron effective-mass ratio m^* from this dispersion relation, one finds that the quantity $[m^*/(1-m^*)]^2$ is linearly related to $n^{2/3}$. If one compares the experimental mean values of $[m^*/(1-m^*)]^2$ with the values predicted theoretically using the best fit values $P=7.1\times10^{-8}$ eV cm and $E_g=0.24$ eV, one finds that for concentrations below 10^{18} cm^{-3} the deviations are random and less than 10% of the experimental error, and less than the experimental error for all concentrations. Thus, we believe that this dispersion relation provides a very good description of the conduction band of HgSe in the range of energy we are considering, indeed considerably better than an extrapolation from Cardona and Harbeke's determination of Δ_1 would indicate.

To invert this expression and find the crystal momentum k and density of states ρ as a function of energy, we follow Ehrenreich[12] and expand to first order in μ the cyclotron effective-mass ratio at the zone center. This yields the following results:

$$k=(2\mu m_0E_g/\hbar^2)^{1/2}s(y), \tag{2}$$

$$\rho=[(2E_g)^{1/2}V(\mu m_0)^{3/2}/8\pi^3\hbar^3]\lambda(y), \tag{3}$$

$$\lambda(y)=[\beta y(1+\beta y)]^{1/2}[1+(2-5\mu)\beta y-8\mu\beta^2y^2], \tag{4}$$

$$s(y)=[\beta y(1+\beta y)]^{1/2}(1-\mu\beta y), \tag{5}$$

$$\mu=(\tfrac{4}{3}m_0P^2/E_g\hbar^2+1)^{-1}, \tag{6}$$

$$y=E/k_BT, \tag{7}$$

$$\beta=k_BT/E_g. \tag{8}$$

k_B is Boltzmann's constant.

The Fermi level E_F and the number of electrons n_e are then found by the solution of the equation

$$n_e-n_h=\sum_i Z_iN_i, \tag{9}$$

where

$$n_e=\frac{1}{2\pi^2}\left(\frac{2\mu m_0k_BT}{\hbar^2}\right)^{3/2}\left[F_{1/2}(z)+\beta(\tfrac{5}{2}-5\mu)F_{3/2}(z)+\beta^2\left(1-\frac{21\mu}{2}\right)F_{5/2}(z)-4\mu\beta^3F_{7/2}(z)\right], \tag{10}$$

$$n_h=\frac{1}{2\pi^2}\left(\frac{2\mu_vm_0k_BT}{\hbar^2}\right)^{3/2}F_{1/2}\left(\frac{E_{g1}}{k_BT}-z\right), \tag{11}$$

$$z=E_F/k_BT. \tag{12}$$

N_i is the number per cm^3 of ions with charge Z_ie. μ_v is the effective-mass ratio of the valence band whose edge lies at E_{g1} measured positively with respect to the conduction-band edge. The $F_i(z)$ are the Fermi functions of half-integral order.[13]

[12] H. Ehrenreich, J. Phys. Chem. Solids **2**, 131 (1956).

[13] J. McDougall and E. C. Stoner, Phil. Trans. Roy. Soc. London **A237**, 350 (1938).

3. VALANCE-BAND OVERLAP

Harman and Strauss[5] have analyzed the temperature dependence of the Hall effect in HgSe. They have found it necessary to assume a 0.07-eV overlap of the valence and conduction bands in order to explain these data. However, in their analysis they used conduction-band parameters which yield a zone-center cyclotron mass ratio of one-fourth that corresponding to Whitsett's parameters. Unfortunately, the amount of overlap required by the Hall data is extremely dependent on the values chosen for the conduction-band parameters.

One would expect a considerably smaller value of overlap using Whitsett's values, since his conduction-band energy rises much more slowly with increasing k than does that of Harman and Strauss. We have used Eqs. (9)–(11) to fit the Hall concentration at 4.2, 77, and 300 K for samples ranging in 4.2 K concentration from 1.5×10^{17} to 4.5×10^{18} cm^{-3}.[14] No freeze-out is seen, and the R_{H77}/R_{H300} for these samples agree with those given by Harman and Strauss. A rather good fit is obtained for $E_{g1}=0.019$ eV and $\mu_v=0.18$, using Whitsett's conduction-band parameters at 4.2 K with a linear variation to the values determined in infrared experiments by Wright, Strauss, and Harman[6] at 300 K. An extremely good fit, even reproducing the small negative curvature of the Hall concentrations above 77 K, can be obtained by assuming the same temperature coefficient as found by Pidgeon and Groves[15] for HgTe. This fit yields a value of E_{g1} less than 0.01 eV and a μ_v of about 1. Unfortunately, in the fitting procedure, E_{g1}, and μ_v are highly correlated. We are expanding the program to include a larger number of temperature points for each sample, and this will be reported on elsewhere.[16] However, it does not seem possible to obtain any fit at all for $E_{g1}>0.02$ eV. Since this energy is smaller than the Fermi energy (as computed using Whitsett's band parameters) for the lowest concentration sample considered in the following, it has no effect on the scattering calculation at 4.2 K. This is not, however, true at higher temperatures.[16]

It should be noted that an overlap this small could be produced by the interband spin-orbit matrix elements, $\langle\Gamma_{12}|\mathcal{H}_{so}|\Gamma_{15}\rangle$, which provide the terms linear in k in the energy of the Λ_4, Λ_5 parts of Γ_8.

4. IONIZED IMPURITY SCATTERING

We consider the scattering of electrons of wave vector $\mathbf{k}$ and wave function $e^{i\mathbf{k}\cdot\mathbf{r}}\chi_{\mathbf{k}}(\mathbf{r})$ by the ith-type of charged impurity. We assume that the interaction energy can be represented by a screened Coulomb

[14] I am indebted to Dr. S. L. Lehoczky for use of his Hall measurements.

[15] C. R. Pidgeon and S. H. Groves, in *Proceedings of the International Conference on II-VI Semiconducting Compounds, Providence, 1967*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1968).

[16] S. L. Lehoczky, C. R. Whitsett, and J. G. Broerman (unpublished).

potential of the form

$$U(r)=-(Z_i e^2/\epsilon r)e^{-ar}, \tag{13}$$

where ϵ is the dielectric constant and a is the reciprocal screening distance. We assume that any overlapping valence electrons are too heavy to screen effectively for the light conduction electrons. We then obtain for the reciprocal screening distance

$$a^2=\frac{e^2}{\pi\epsilon}\left(\frac{2\mu m_0}{\hbar^2}\right)^{3/2}(k_BT)^{1/2}[q_1^{1/2}(z)+\eta q_2(z)]^2, \tag{14}$$

$$q_1(z)=F_{-1/2}(z)+3\beta(\tfrac{5}{2}-5\mu)F_{1/2}(z)+5\beta^2\left(1-\frac{21\mu}{2}\right)F_{3/2}(z)-28\mu\beta^3F_{5/2}(z), \tag{15}$$

$$q_2(z)=2\frac{dF_{-1/2}(z)}{dz}+3\beta(\tfrac{5}{2}-5\mu)F_{-1/2}(z)+15\beta^2\left(1-\frac{21\mu}{2}\right)F_{1/2}(z)-140\mu\beta^3F_{3/2}(z), \tag{16}$$

$$\eta=\frac{Z_ie^3}{16\pi^{1/2}\epsilon^{3/2}}\left(\frac{2\mu m_0}{\hbar^2k_BT}\right)^{3/4}. \tag{17}$$

The first term in the square brackets of (14) yields the conventional Fermi-Thomas screening distance for this band structure. The second term is the Friedel correction[17] modified for a material with dielectric constant ϵ and evaluated for this band structure.

For our band structure, which ignores warping and the asymmetry splittings discussed by Roth *et al.*,[11] the contribution to the Boltzmann equation from this scattering process is, in the first Born approximation,

$$\left(\frac{\partial f(\mathbf{k})}{\partial t}\right)_{\text{coll}}=\frac{\pi N_iZ_i^2}{\hbar}\frac{e^4}{\epsilon^2}\frac{1}{E_g}\frac{\lambda}{s^3}\frac{\partial f_0}{\partial E}[c(E)\cos\theta]\Phi, \tag{18}$$

$$\Phi=\int_{-1}^{1}\frac{2k^4}{[a^2+|\mathbf{k}-\mathbf{k}'|^2]^2}\times\sum_{\mu\mu'}\left|\int\chi_{\mathbf{k}\mu}^*(\mathbf{r})\chi_{\mathbf{k}'\mu'}(\mathbf{r})d^3\mathbf{r}\right|^2(1-x)dx. \tag{19}$$

In these expressions, θ is the angle between an applied electric field and the wave vector, $\mathbf{k}$ and $\mathbf{k}'$ are the initial and final wave vectors, x is the cosine of the scattering angle, $\chi_{\mathbf{k}\mu}(\mathbf{r})$ is the cell-periodic part of the wave function, $f(\mathbf{k})$ and $f_0(E)$ are, respectively, the perturbed and unperturbed electron distribution functions, and $C(E)$ is defined by

$$f(\mathbf{k})=f_0(E)-kc(E)\cos\theta\,\partial f_0(E)/\partial E. \tag{20}$$

The sum over μ, μ' is a result of the neglect of asymmetry splittings, so that every $\mathbf{k}$ has two states associated with it, each with the same energy. If this scattering mechanism is the limiting one, (18) yields the conductivity

$$\sigma=\frac{2}{3\pi^3\hbar}\left(\frac{2\mu m_0}{\hbar^2}\right)E_g^3\frac{\epsilon^2}{e^2}\frac{1}{N_iZ_i^2}\int_0^\infty\frac{e^{y-z}}{(e^{y-z}+1)^2}\frac{s^8}{\lambda^2\Phi}dy. \tag{21}$$

If $\chi_{\mathbf{k}}(\mathbf{r})$ is a pure s-like function, (21) yields the usual Brooks-Herring formula, modified for a nonparabolic band shape. However, whether the conduction-band edge is Γ_6 or Γ_8, the wave function at the Fermi surface will contain some p-like contribution (for nonzero electron concentration) and this will vary as the Fermi level is varied. Using Kanes' results,[9] one can show for either Γ_8 or Γ_6 band edges

$$\tfrac{1}{2}\sum_{\mu\mu'}\left|\int\chi_{\mathbf{k}\mu}^*\chi_{\mathbf{k}'\mu'}d^3r\right|^2=\sum_{i=0}^{2}\pi_ix^i, \tag{22}$$

where the π_i depend on the symmetry of the band edge and are functions of y. Φ is then found to be

$$\Phi=\sum_{i=0}^{2}\pi_i\phi_i,\quad \gamma=\frac{4\pi\epsilon}{e^2}\left(\frac{\hbar^2}{2\mu m_0k_BT}\right)^{1/2}\frac{E_g}{(q_1^{1/2}+\eta q_2)^2}, \tag{23}$$

$$\phi_0=\ln|1+\gamma s^2|-\gamma s^2/(1+\gamma s^2), \tag{24}$$

$$\phi_1=\frac{4+\gamma s^2}{\gamma s^2}\ln|1+\gamma s^2|-\frac{4+3\gamma s^2}{1+\gamma s^2}, \tag{25}$$

$$\phi_2=\frac{1}{\gamma s^2}\left(-2(4+\gamma s^2)+\frac{(2+\gamma s^2)(6+\gamma s^2)}{\gamma s^2}\times\ln|1+\gamma s^2|-\frac{(2+\gamma s^2)^2}{(1+\gamma s^2)}\right). \tag{26}$$

The π_i now contain all the effects of band-edge symmetry. If the band edge is of Γ_8 symmetry, the expressions for the π_i are

$$\pi_0=\frac{1}{(2\beta y'+1)^2}\left(\frac{(\beta y'+1)^2}{4}+\frac{(1-\mu)^2s^4(y)}{(\beta y'+1)^2}\right), \tag{27}$$

$$\pi_1=2(1-\mu)s^2(y)/(2\beta y'+1)^2, \tag{28}$$

$$\pi_2=\tfrac{3}{4}[(\beta y'+1)/(2\beta y'+1)]^2, \tag{29}$$

$$y'=y-\beta^{-1}\mu s^2(y). \tag{30}$$

If the band edge is of Γ_6 symmetry, the expression for π_1 is still given by (28), while π_0 and π_2 are given by

$$\pi_0=\frac{1}{(2\beta y'+1)^2}\left((\beta y'+1)^2+\frac{1}{4}\frac{(1-\mu)^2s^4(y)}{(\beta y'+1)^2}\right), \tag{31}$$

$$\pi_2=\tfrac{3}{4}(1-\mu)^2s^4(y)/(2\beta y'+1)^2(\beta y'+1)^2. \tag{32}$$

[17] J. Friedel, Advan. Phys. 3, 446 (1954).

For low temperature or large z, the integral (21) can be approximately evaluated in the usual manner. The results are easily obtained and will not be given here. A rough summary of the differences in mobility for the two symmetry types can be given as follows. For the same band shape, the calculated mobility for a band with a Γ_8-type edge is always greater than that for a band with a Γ_6-type edge. The calculated mobility for a Γ_8-type band increases more rapidly with decreasing electron concentration than that for a Γ_6-type band. These results will be compared with Whitsett's measured mobilities in Sec. 5.

5. RESULTS AND CONCLUSIONS

It is believed that the crystals used in Whitsett's experiment contain a very small number of acceptor-type impurities.[18] We will assume that there is one species of donor present and that it is singly ionized. We will also assume that scattering from these impurities is the limiting mechanism in electrical conduction at 4.2 K, which is quite reasonable for this temperature and range of concentrations. Whitsett's values for the band parameters, $P=7.1\times10^{-8}$ eV cm and $E_g=0.24$ eV, are used with a dielectric constant[19] of 25.6. The resulting calculated Hall mobilities as a function of concentration for the two band types are plotted in Fig. 1 along with Whitsett's experimental values. As can be seen, the results for the Γ_8-type band are in excellent agreement with the experimental values, while those calculated for a Γ_6-type band are both too low and rise too slowly with decreasing electron concentration.

At this point we would like to make some comments on the validity of this calculation. First, it should be noted that we are in a range of concentration, effective mass, and dielectric constant for which the Born approximation should be quite accurate.[20] Oddly enough, errors associated with the Born approximation in degenerate semiconductors in this range of these parameters tend to overestimate the mobility. Second, at the highest concentration we may be entering a region in which multiple-scattering processes will contribute to the total scattering cross section. Their inclusion would lower the calculated mobility. Third, including the effect of acceptors or other impurities in the material would also lower the calculated mobility. Thus, we believe that this calculation is accurate and provides an upper limit to more rigorous calculations using Whitsett's band-structure parameters.

The difference in mobility between Γ_6 and Γ_8 band edges is even more striking at lower concentrations where the band mixing is not so strong. Long[21] has recently performed a calculation of the low-temperature

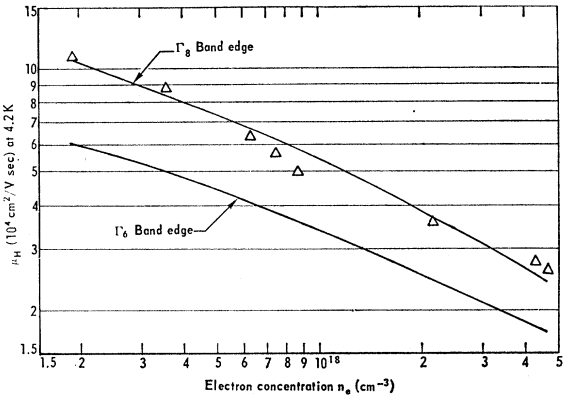

FIG. 1. Hall mobility of mercuric selenide as a function of conduction-electron centration at 4.2 K calculated for Γ_6 and Γ_8 band-edge symmetries. Triangles are Whitsett's experimental values (Ref. 1).

mobility in the Born approximation for n-type Hg_{1-x} Cd_x Te, ignoring the angular dependence of the Γ_8 matrix elements. In this system, as one varies x from 0 to 1, the band structure goes from the inverted gray-tin structure smoothly into the standard germanium structure. The asymmetry in the mobility as a function of x about the crossover value of x should be quite marked if one includes the effects of band symmetry. However, at the electron concentrations considered by Long, one would probably have to perform a phase-shift calculation for the angular cross section. We are attempting to include the angular variation of the cell-periodic part of the wave function in a phase-shift calculation.

We are also performing a calculation of the high-temperature mobility of HgSe, including the effect of screening and the cell-periodic effect on polar optical scattering of electrons.[16]

In summary, we believe that the excellent agreement between Whitsett's mobilities and the values calculated using his band parameters provides a good consistency check on his band model. Alternatively, accepting Whitsett's band parameters, the agreement with the values calculated for Γ_8 band-edge symmetry and lack of agreement for Γ_6 symmetry argues strongly for the inverted, gray-tin structure.[10] The lower value obtained for the valence-band overlap using Whitsett's conduction-band parameters would then be consistent with the overlap of the Λ_4, Λ_5 parts of Γ_8 caused by the terms in their energy linear in k at the zone center.

ACKNOWLEDGMENTS

I would like to thank E. C. Paxhia for his programming of the Fermi level and mobility calculations. I would like to thank Dr. S. L. Lehoczky for the use of his Hall data. Finally, I would like to thank Dr. C. R. Whitsett for many stimulating discussions on both the theoretical and experimental aspects of work on mercuric selenide.

[18] C. R. Whitsett (private communication).
[19] Z. I. Kiriashkina *et al.*, Zh. Tekhn. Fiz. **27**, 85 (1957) [English transl.: Soviet Phys.—Tech. Phys. **2**, 69 (1957)].
[20] J. B. Krieger and S. Straus, Phys. Rev. **169**, 674 (1968).
[21] D. Long, Phys. Rev. **176**, 923 (1968).