Magnetic Breakdown and the Spin-Split Conduction Band in HgSe and $Hg_{1-x}Mn_xSe$

R. Reifenberger and D. A. Schwarzkopf
Department of Physics, Purdue University, West Lafayette, Indiana 47907
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New measurements of the anomalous magnetic field dependence in the amplitude of the oscillatory magnetoresistance (Shubnikov–de Haas effect) of n-type HgSe and $Hg_{1-x}Mn_xSe$ are presented. These data are interpreted with use of a closed-orbit magnetic breakdown model which permits Fermi-surface parameters of interest to be determined. It is found that the addition of 0.1-at.% Mn to HgSe results in a Fermi surface whose shape is temperature dependent.

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Alloys formed by the substitution of magnetic Mn^{++} ions in HgSe have been the subject of recent study because of their interesting electrical, optical, and magnetic properties.[1-6] These ternary alloys crystallize in the zinc-blende crystal structure and display unusual magnetic effects due to the exchange interaction between the magnetic Mn^{++} ions and the band electrons. Although some investigators have reported anomalous behavior in the quantum oscillatory transport properties in these materials,[7,8] there has been no systematic use of this effect to study the changes in the band structure of HgSe due to the addition of Mn^{++}.

As is known from group-theoretical arguments, the conduction band in any zinc-blende semiconductor is split because of the lack of inversion symmetry.[9,10] Evidence for this splitting was found in the anomalous line shape of the magnetoresistance oscillations in n-type HgSe.[11] Subsequent work in GaSb[12] and HgSe[13] provided further evidence that for certain values of the applied field, the amplitude of the magnetoresistance oscillations anomalously went through zero. Theoretical work[14,15] showed that the magnetic field dependence of the quantum oscillations could be semiquantitatively explained with use of a Hamiltonian that described the inversion asymmetry of the lattice.

From these prior investigations it was realized that magnetic breakdown effects play an important role in the quantum oscillatory properties of inversion-asymmetric semiconductors. However, no theory has been presented which exploits this insight to yield quantitative information about the spin splitting of the conduction band. This paper describes the consistent model necessary to determine such information for any zinc-blende semiconductor. We use this model to analyze new data from $Hg_{0.999}Mn_{0.001}Se$ and contrast the results to those obtained from HgSe.

When magnetic breakdown effects are important, the oscillatory magnetoresistance in semiconductors and simple metals which have a Fermi surface that does not intersect any Brillouin zone boundary is given by

$$\frac{\Delta\rho}{\rho_0} \propto \sum_r \frac{(-1)^r H^{1/2} A_r B_r K_r X_r}{r^{1/2}\sinh X_r} \cos(\pi r S)\cos\left(\frac{2\pi r F}{H}+\chi\right), \tag{1}$$

where H is the applied magnetic field; A_r is constant related to the shape of the Fermi surface; $K_r=\exp(-\alpha r T_D/H)$ ($\alpha=2\pi^2 m^* k_B/e\hbar$) with T_D, the Dingle temperature, being a measure of the impurity/dislocation scattering in the material; $X_r/\sinh X_r$ ($X_r=\alpha r T/H$) is a thermal damping factor at a temperature T; and $\cos(\pi r S)$ ($S=gm^*/2m_0$) incorporates the effective cyclotron-averaged g factor and effective mass (m^*) of the electrons. The extremal area A of the Fermi surface is related to the frequency F by the Onsager formula $F=\hbar A/2\pi e$. The factor B_r introduces magnetic breakdown effects and is the term of interest here. It is well established that Eq. (1) or its de Haas–van Alphen equivalent can be used to investigate both the details of the energy band structure near the Fermi energy and the k-dependent scattering of the conduction electrons in metals and semiconductors.[16]

For our calculations, a model of the Fermi-surface geometry of HgSe is used that gives the Fermi wave vectors k_F in terms of known functions based on Kane's three-band approximation.[13,17] In what follows, we concentrate on the Fermi-surface cross section for $H \parallel [111]$ as shown in Fig. 1. The position of the magnetic breakdown junctions, corresponding to the points of minimum separation between the two orbits, are indicated by the six circles in this figure.

The difference in area between the two spin-split surfaces is given by 6Δ.

To calculate the magnetic field dependence in the amplitude of the magnetoresistance oscillations, we must assign a breakdown probability amplitude $p=\exp(-H_0/2H)$ and reflection probability amplitude $q=i(1-p^2)^{1/2}$ for an electron state to either tunnel or reflect from each breakdown junction.[18] The breakdown field H_0 is given by

$$H_0=\pi m^* E_g^{\,2}/(e\hbar E_F \sin\Phi), \tag{2}$$

where E_g is the splitting between the conduction bands and Φ is the angle through which the electron state is turned upon reflection from the breakdown junction.

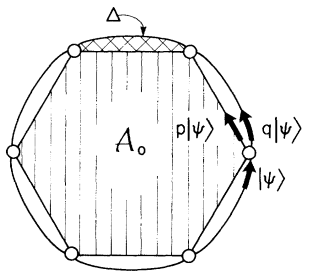

FIG. 1. Schematic diagram of the extremal cross-sectional area of the Fermi surface in HgSe for $H \parallel [111]$. The evolution of the state $|\psi\rangle$ at a magnetic breakdown junction is also shown.

A propagator formalism[19,20] has been used to calculate the correct combination of p's and q's for each of the 2^6 orbits that comprise the fundamental harmonic ($r=1$) and 2^{12} orbits that give rise to the second-harmonic content ($r=2$) for $H \parallel [111]$. The breakdown function B_1 for the fundamental harmonic is found to be

$$B_1=2q^6\cos\left(\frac{6\pi F_\Delta}{H}\right)+12q^4p^2\cos\left(\frac{4\pi F_\Delta}{H}\right)+(12q^4p^2+18q^2p^4)\cos\left(\frac{2\pi F_\Delta}{H}\right)+(6q^4p^2+12a^2p^4+2p^6), \tag{3}$$

where $F_\Delta=\hbar\Delta/2\pi e$, and where F in Eq. (1) is given by $F=\hbar(A_0+3\Delta)/2\pi e$. A similar but more complicated formula for the second-harmonic term has also been obtained.[19]

As is evident from Eq. (3), a number of zeros are introduced into the amplitude of the fundamental harmonic (and all higher harmonics) of the magnetoresistance oscillations. Most importantly, the values of H at which these zeros occur give a *direct* experimental measure of the two parameters of interest, Δ and H_0, both of which can be predicted from band-structure calculations.

This result is easily seen for the fundamental harmonic by considering Eq. (3) in two limits. For $H \ll H_0$, $|p|\to 0$, $|q|\to 1$, and the breakdown factor B_1 reproduces the expected result for two uncoupled orbits on the Fermi surface:

$$B_1 \simeq 2\cos(6\pi F_\Delta/H). \tag{4}$$

Equation (4) predicts a number of low-field zeros in the amplitude of the fundamental harmonic at magnetic fields satisfying the following condition:

$$H=12F_\Delta/(2n+1); \quad n=0,1,2,\ldots. \tag{5}$$

In the high-field limit when $H \gg F_\Delta$, the cosine factors in Eq. (3) can be approximated by constants very near to unity and B_1 is then given by

$$B_1 \simeq 2q^6+30q^4p^2+30q^2p^4+2p^6. \tag{6}$$

It can be shown that for a given H_0 there are only three values of the magnetic field that make B_1 in Eq. (6) equal to zero. These values of H are given by

$$H_1=14.422H_0; \quad H_2=1.443H_0; \quad H_3=0.370H_0, \tag{7}$$

where the numerical constants result from the three real roots of Eq. (6). At fields for which neither $H \ll H_0$ nor $H \gg F_\Delta$, the position of the zeros in both the fundamental and the second harmonics are not easily written in closed form but can be found by numerical techniques.

This model has been used to analyze Shubnikov–de Haas data recently obtained from both HgSe and $Hg_{1-x}Mn_xSe$. Figure 2 is a plot of the measured magnetic field dependence of the fundamental and second-harmonic amplitudes found in the transverse magnetoresistance oscillations obtained for a single crystal of HgSe with $H \parallel [111]$. The amplitude decomposition of the magnetoresistance oscillations was performed with use of least-squares–fitting techniques.[19] The value of $H=0.8$ T at which the zero in the amplitude of the fundamental harmonic is observed is in good agreement with previous measurements.[13]

Two parameters are adjusted in order to bring the predictions of the theory into accord with experiment: the value of the magnetic breakdown parameter H_0 and the difference area Δ. From Fig. 1, the quantity 6Δ measures the difference in area between the two extremal orbits while H_0 describes the probability of an electron to tunnel between the two sheets of the Fermi surface.

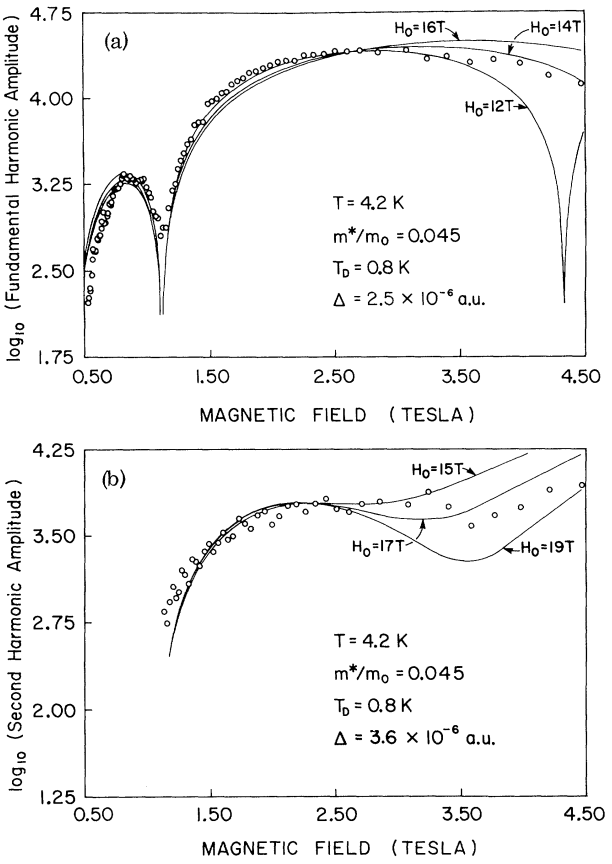

FIG. 2. Magnetic field dependence of the (a) fundamental and (b) second-harmonic amplitudes measured for the transverse magnetoresistance oscillations for $H \parallel [111]$ in HgSe ($n \simeq 4.8\times 10^{17}$ cm^{-3}). The theoretical fits based on Eq. (1) are also shown.

The effective mass has been determined with use of standard techniques and was found to be $m^* \simeq 0.045 m_0$. The Dingle temperature T_D appearing in Eq. (1) acts as a general shape parameter that controls how quickly the harmonic amplitudes increase with magnetic field. The estimated uncertainties in the values required to fit these data are $H_0 = (16 \pm 2)$ T and $\Delta = (3.0 \pm 0.5) \times 10^{-6}$ a.u. On the basis of this nominal value for H_0, we can estimate the size of the inversion-asymmetry gap in HgSe, giving $E_g \simeq 0.11(\sin\Phi)^{1/2} \times E_F^{1/2}$ (E_g and E_F in electronvolts). It is important to note that the zero observed in our data cannot be reproduced in any way by the $\cos(\pi r S)$ term in Eq. (1), since there is no evidence for a magnetic-field–dependent g factor in HgSe.

The results of a similar analysis on data from $Hg_{0.999}Mn_{0.001}Se$ are presented in Fig. 3 and show changes to the Fermi surface that have resulted from the addition of Mn^{++}. It is found that al-

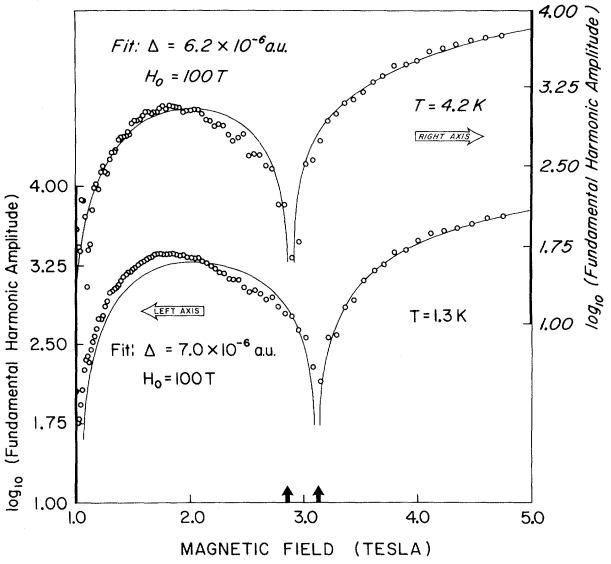

FIG. 3. Temperature dependence in the amplitude of the fundamental harmonic in $Hg_{0.999}Mn_{0.001}Se$ for $H \parallel [111]$ with $n \simeq 1.8\times 10^{18}$ cm^{-3}. The temperature-dependent shift of the zero in the fundamental harmonic by 0.23 T is indicated by the arrows.

though the value of the breakdown field H_0 has increased beyond our range of accurate measurement, the difference area Δ, which is determined mined by the field of the observed zero, is ~1.2 times the value expected for a HgSe sample of comparable electron concentration. The latter result provides good evidence that the zero in the magnetoresistance oscillations obtained in the $Hg_{0.999}Mn_{0.001}Se$ system must have the same origin as found for the zero in HgSe. This is important because it indicates quite clearly that the line shape of the magnetoresistance data from $Hg_{0.999}Mn_{0.001}Se$ does not contain spin-splitting features attributable to zeros in the $\cos(\pi r S)$ term in Eq. (1) as postulated previously in both Refs. 7 and 8. Although this conclusion is based on the $H \parallel [111]$ data presented here, similar conclusions follow from a study of data on $Hg_{0.999}Mn_{0.001}Se$ taken for different orientations of the applied magnetic field.

From Fig. 3 we also find that the presence of Mn^{++} causes the value of Δ to vary with temperature, indicating a temperature-dependent splitting between the conduction bands. No such behavior is observed in HgSe where the positions of the zeros in the amplitude of the fundamental harmonic remain constant with temperature. Although our data do not allow us to identify the microscopic origin of this temperature-dependent splitting, it presumably can be attributed to a

temperature-dependent spin-orbit coupling term in the Hamiltonian used to calculate the energy band structure for the $Hg_{1-x}Mn_xSe$ system.

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Selection Rules and Multiplet Effects in Comparison of X-Ray Absorption and Photoemission Peak Energies

J.-M. Esteva and R. C. Karnatak

Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, F-91405 Orsay Cédex, France, and European Research Associates 719, Université de Paris-Sud, F-91405 Orsay Cédex, France

and

J. C. Fuggle

Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, West Germany

and

G. A. Sawatzky

Institute for Physical Chemistry, University of Groningen, 9747AG Groningen, The Netherlands

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Measurements of the La 3*d* binding energies as studied by x-ray photoelectron and x-ray absorption spectroscopies are reported. Apparent discrepancies of ~ 2–3 eV in the observed peak energies are shown to be due to the d^9f^n multiplet splittings and the different selection rules in the different spectroscopies. It is argued that these effects have a wider relevance to solid systems with strongly localized, open-shell electrons, such as rare earths and transition-metal compounds.

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This paper concerns apparent discrepancies between binding energies found in different core-level spectroscopies. In the course of x-ray photoemission (XPS) and x-ray absorption (XAS) studies of the 3*d* levels in La and Ce intermetallic compounds we realized that there was a disagree-