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Location of the ⟨111⟩ Conduction Band Minima in the $Ga_xIn_{1-x}Sb$ Alloy System

Abstract: Pressure dependence of the resistivity and optical absorption by conduction band electrons are used to determine the position of the ⟨111⟩ (L_1) conduction band minima in the Ga_xIn_{1-x} Sb alloy system. These experimental data permit a more precise estimate of the position of the L_1 minima than had been possible using Gunn effect data alone.

Introduction

Recent observations of the Gunn effect in the $Ga_xIn_{1-x}Sb$ alloy system[1] for $0.3 \leq x \leq 0.54$ have been interpreted in terms of a conduction band model for this alloy system. In this model, above the lowest lying Γ_1 conduction band minimum the next lowest set of minima is the L_1 set throughout the alloy system. This paper reports two types of experiments which provide a more precise determination of the energy of these L_1 minima relative to the Γ_1 minimum. In the first experiment hydrostatic pressure is used to reduce the energy separation between the two sets of minima. The resulting increase in resistivity at high pressure due to occupation of the L_1 minima is analyzed to deduce the energy separation at atmospheric pressure. The second experiment is a study of the optical absorption due to transitions by electrons within the conduction band.

Pressure dependence of resistivity

For all compositions x the lowest conduction band minimum in the $Ga_xIn_{1-x}Sb$ alloy system is the light mass Γ_1 minimum.[2] Because of the small effective mass, electrons in this minimum are expected to have a rather high mobility.

By analogy with the other Ge-family semiconductors,[3] the application of hydrostatic pressure is expected to reduce the energy separation between the Γ_1 and L_1 conduction band minima at a rate of 1×10^{-5} eV/bar. At a pressure sufficiently high that this energy separation is a few times kT, where T is the lattice temperature and k is Boltzmann's constant, the conduction electrons will be shared between the Γ_1 and L_1 minima. Since the mobility of an electron in an L_1 minimum is much smaller than in the Γ_1 minimum, this population shift results in a rapid increase of resistivity with pressure.

In this alloy system, the conduction band ordering is: Γ_1 lowest in energy, followed by L_1, and then X_1 or Δ_1 min. With this ordering an additional complication can be present. Hydrostatic pressure lowers the energy of the X_1 minima relative to Γ_1 at a faster rate ($\approx 1.5 \times 10^{-5}$ eV/bar) than it lowers the L_1-Γ_1 separation.[3] Thus, even though at atmospheric pressure the L_1 are the second lowest conduction band minima, if the X_1 minima are not far above the L_1 minima, the application of sufficient pressure may in fact bring the X_1 minima below the L_1 minima.

Two-terminal resistance measurements were performed on n-type $Ga_xIn_{1-x}Sb$ samples for compositions x of 0.3 and 0.5. The samples were the same ones on which the Gunn effect measurements[1] had been made. Pressures up to 28 kilobars were used, and the measurements were done at room temperature. The samples were not totally extrinsic until pressures of a few kilobars were applied. Raising the pressure above this value resulted in a linear increase in resistance until much higher pressures—about 15 kilobars for $Ga_{0.5}In_{0.5}Sb$, and 20 kilobars for $Ga_{0.3}In_{0.7}Sb$. Above these pressures the resistance of the samples increased much more rapidly than linearly, indicating the increasing population of lower mobility minima. The data for a sample of $Ga_{0.5}In_{0.5}Sb$ are shown in Fig. 1.

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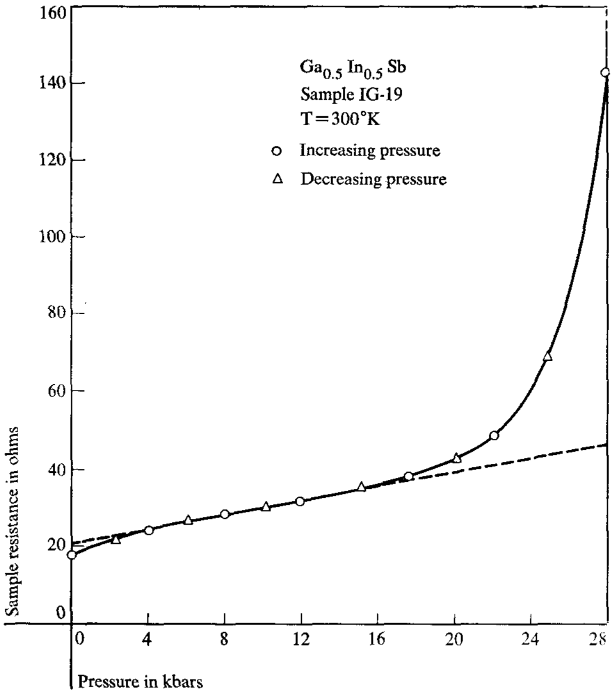

Figure 1 Typical variation of sample resistance with pressure. The data are for a sample of $Ga_{0.5}In_{0.5}Sb$. The straight line is taken to represent the part of the resistivity increase due to the variation of central valley mobility with pressure.

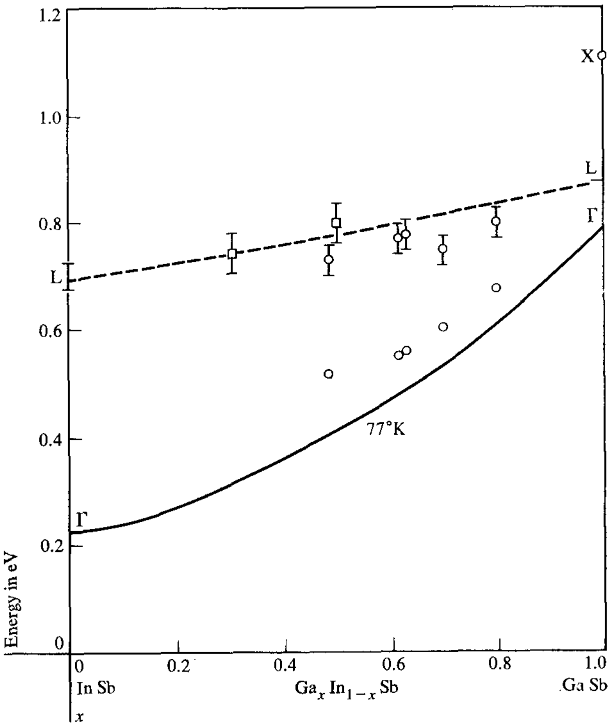

Figure 2 The conduction band structure of the $Ga_xIn_{1-x}Sb$ alloy system. The lower curve represents the fundamental energy gap at 77°K. The circled points correspond to E_G' (see Fig. 3). The solid points with vertical error bars correspond to the sum of $E_G' + E_0$ and they define the energy position of the L_1 minima relative to the valence band energy, taken as zero. The two squared points define the L_1 minima as found from hydrostatic pressure measurements.

In order to analyze the data the following assumptions were made: (a) The initial increase of resistivity with pressure (below 5 kilobars in Fig. 1) is due to a rapid reduction of intrinsic carrier density with increasing energy gap; (b) in the middle pressure range, the linear variation of resistivity with pressure reflects the reduction of the central valley mobility with increasing energy gap; and (c) the rapid additional increase in resistivity at high pressure (above 15 kilobars in Fig. 1) is due to the transfer of an increasing fraction of the electrons to subsidiary conduction band minima where their mobility is negligible compared to the central valley mobility. Since there is no degeneracy, the populations of the two types of minima are related by a Boltzmann factor

$$n_L/n_\Gamma = R \exp\left[-\Delta(P)/kT\right], \qquad (1)$$

where R is the ratio of the densities of states in the two types of minima and $\Delta(P)$ is the energy separation at pressure P.

Determination of the energy separation at atmospheric pressure, Δ(1 bar), requires a knowledge of the pressure coefficient of Δ, $\partial\Delta/\partial P$, which one would hope to obtain by evaluating $\Delta(P)$ at several pressures using Eq. (1). It should be mentioned that the values of Δ(1 bar) and $\partial\Delta/\partial P$ are rather insensitive to the particular value of the density of states ratio R which is used. The final error estimate includes a variation of R from 20 to 100. The data for $Ga_{0.5}In_{0.5}Sb$ provide a mean value of $\partial\Delta/\partial P = 1.0 \times 10^{-5}$ eV/bar in good agreement with the value expected,[3] assuming that the relevant low mobility minima are of L_1 symmetry, so that the extrapolation to atmospheric pressure can be confidently made. The pressure coefficient $\partial\Delta/\partial P$ for $Ga_{0.3}In_{0.7}Sb$ cannot be determined with precision from the data. In this case we have assumed that the X_1 minima *have not* crossed the L_1 minima—that is, that the X_1 minima lie at least 0.15 eV above the L_1 minima at atmospheric pressure. A pressure coefficient $\partial\Delta/\partial P = 1 \times 10^{-5}$ eV/bar is then used for the extrapolation to atmospheric pressure from the value of Δ determined from the data at 26 kilobars, which include the effect of a substantial repopulation. The final errors quoted include a possible 10% uncertainty in this pressure coefficient. The room temperature values of Δ(1 bar) obtained in this way are shown below.

$Ga_{0.3}In_{0.7}Sb$: $\Delta(1\ \text{bar}) = 0.40 \pm 0.05$ eV
$Ga_{0.5}In_{0.5}Sb$: $\Delta(1\ \text{bar}) = 0.36 \pm 0.05$ eV

To compare these values with the optically determined positions of the L_1 minima at 77°K discussed below, we must estimate the change in the above values on going from room temperature to 77°K. In the absence of any measurements of the temperature variation of the position of the L_1 minima in these alloys, we have assumed that the L_1—valence band separation will increase by 0.08 eV when the temperature is reduced from 300°K to 77°K. This is the temperature variation of the relative positions of the same pair of bands in germanium. In Fig. 2 the square points and associated error bars are the results of this procedure.

Optical absorption

If the energy difference between the L_1 and Γ_1 conduction band minima is less than E_G, their energy separation can be deduced from optical absorption of free electrons. Such interband absorption was previously observed in n-type GaAs by Spitzer and Whelan[4] and in n-type InP by Lorenz et al.[5] The dominant absorption processes are shown schematically in the inset of Fig. 3. To observe the free carrier absorption an appreciable occupation of the conduction band is required. Analysis of the interband free carrier absorption, α_{IB}, yields E_0, which can then be related to the energy separation of the conduction bands.

To determine the conduction band structure from optical absorption we used n-type material doped with Te to a concentration of about 10^{18} cm^{-3}. This is in contrast to the hydrostatic pressure measurements, which were made on lightly doped ($\approx 10^{15}$ cm^{-3}) n-type material. The doped samples were grown by passing a molten zone through a cast ingot of starting composition corresponding to 50 mole-percent InSb and 50 mole-percent GaSb. The end of the ingot frozen first was GaSb-rich and the other end was nearly pure InSb.

Various slices corresponding to different compositions were chosen. The composition of each slice was then analyzed chemically by atomic absorption, and by x-ray powder diffraction. The carrier concentration was determined from Hall measurements on van der Pauw samples. Carrier concentrations ranged from 4×10^{17} cm^{-3} in the GaSb-rich samples to 1.7×10^{18} cm^{-3} in the InSb-rich samples. The major part of each slice was mechanically polished for optical transmission studies. Sample thicknesses ranged between 0.014 and 0.018 cm.

The optical transmission of samples at 77°K was measured as a function of photon energy from 0.1 eV to near total absorption at the energy gap. The absorption coefficient α was determined from the expression

$$T = \frac{(1 - R^2)e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}}, \qquad (2)$$

where T is the transmission, R is the reflectivity and d the sample thickness. A constant value of 0.35 was used for the reflectivity for all alloy compositions. The absorption coefficient as a function of photon energy for one of the samples is shown in Fig. 3. The absorption coefficient at low photon energy corresponds to the normal free carrier absorption, α_{FC}. The free carrier absorption was extended to higher energy and the extrapolated curve (α_{FC}) is shown in Fig. 3. When α_{FC} is subtracted from the total absorption, the solid curve marked α_{IB} is obtained. This curve is interpreted as being due to the interband free carrier absorption, which corresponds to raising electrons from the Γ_1 minimum to the L_1 minima. The onset of this absorption occurs approximately when the photon energy is large enough to raise an electron from the Fermi level in the Γ_1 band to the bottom of the L_1 band. We neglect the energy of the phonon involved in this indirect process; this introduces a small error in the determination of the separation of the Γ_1 and L_1 minima.

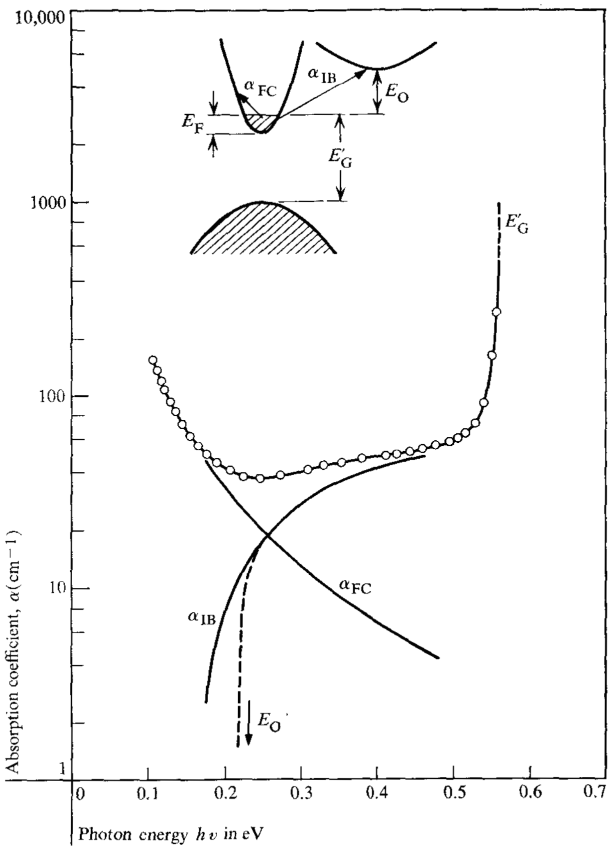

Figure 3 Optical absorption α vs photon energy $h\nu$ at 77°K for an alloy composition of $Ga_{0.63}In_{0.37}Sb$. Sample thickness was 0.014 cm. The circled points correspond to the total measured absorption which is broken up into α_{FC}, the normal free carrier absorption and α_{IB}, the interband free carrier absorption. A schematic diagram of the various absorption processes is shown in the insert.

The interband free carrier absorption is expected to follow an expression[5]

$$\alpha_{IB} = B(h\nu - E_0)^{\frac{1}{2}}, \tag{3}$$

where E_0 is the threshold energy for the absorption. This dependence of α_{IB} is consistent with the assumption that the transition probability is constant between states in the Γ_1 minimum and the L_1 minima and that the electrons occupy states within a range of energy small compared to $(h\nu - E_0)$.[5] The α_{IB} curves for the various compositions were fitted to the above expression by plotting α^2 vs $h\nu$. A straight-line plot was obtained in all cases except at low absorption coefficients, where the observed absorption coefficients were somewhat higher than predicted by Eq. (3). The deviation at small energies occurs because E_F is not negligible relative to $h\nu$. The best fit to the experimental curve is shown in Fig. 3 where the dotted α_{IB} curve corresponds to the best fit and is extremely good for $h\nu$ between 0.25 and 0.45 eV.

The sharp rise of the absorption coefficient at high photon energy corresponds to the onset of valence-band to conduction-band transitions. Since the conduction band is filled up to E_F, the band edge absorption is shifted to higher energy.[6] We extrapolate α to 10^3 cm^{-1} and assume that the corresponding energy is $E_G' = E_G + E_F$. E_G' values for the various compositions studied are shown in Fig. 2. They lie between 70 and 110 meV above the energy gap of the undoped material. This Burstein shift is in reasonable agreement with the Fermi energies deduced from the carrier concentration measurements. Thus from the optical measurements we can obtain the energy difference between the valence band and the L_1 valleys by summing E_G' and E_0. The values of E_G' and $E_G' + E_0$ are plotted in Fig. 2 for the alloy system. The latter points contain error bars of ±30 meV, which is the estimated uncertainty of the energy determination. There is an additional uncertainty of ±2% based on the accuracy of the determination of the chemical composition. The variation of E_G' and $E_G' + E_0$ in the alloy system with position in the ingot is reasonable, and the position in energy of the L_1 minima in the alloys as determined from the optical measurements is in good agreement with the model and the known position of the L_1 minima in GaSb.[7]

Discussion

Figure 2 shows the position of the L_1 conduction band in the mixed crystal system as determined here. These data are clearly consistent with the L_1 minima's being the second lowest set throughout the alloy system, and they provide a more precise estimate of the position of the L_1 minima than was possible using the Gunn effect data alone. The positions determined from the resistivity-pressure data seem to lie higher than those determined optically. As mentioned previously, the resistivity data were taken on lightly doped samples at room temperature, whereas the optical data were taken on heavily doped samples at 77°K. The difference may be due to inaccuracy in correcting for the temperature change discussed above. On the other hand, by analogy with other materials,[8] it might be expected that large donor concentrations introduce significant densities of band-tail states, which may account for the difference between the two results.

Acknowledgments

We are happy to acknowledge the contributions of D. McLeod, who performed the hydrostatic pressure measurements, of G. D. Pettit, who obtained the optical data, and of W. Reuter, who provided the chemical analyses. We are also grateful to J. Angilello for x-ray measurements and to F. R. Feigel, Jr., J. A. Kucza and A. H. Parsons for sample preparation and characterization.

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Received May 9, 1969