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Pressure-dependent compensation in InSb

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High-purity *n*-type InSb exhibits an unusual temperature dependence in the Hall coefficient for pressures in excess of about 8 kbar. The behavior is explained using nonequilibrium semiconductor statistics and a model incorporating shallow donor and deep acceptor states. The best fit to experimental results is accomplished when the assumed number of acceptors exceeds the number of donors, although the material remains *n* type. Below 100 K, equilibrium is not achieved and the number of ionized acceptors is "frozen in" and replaces the total number of acceptors. This gives an apparent ratio of acceptors to donors very close to one. This model could explain, therefore, what appears to be fortuitously close compensation in many high-resistivity materials.

INTRODUCTION

High-resistivity samples of a particular semiconductor appear to be highly compensated with at least one donor level and one acceptor level. Most exhibit metastable characteristics in their thermal and optical properties. While InSb as is *not* normally thought of as high-resistivity material, Porowski and co-workers[1-3] first reported an unusual increase in the Hall coefficient R_H of high-purity extrinsic *n*-type InSb as temperature was lowered for pressures in excess of 7–8 kbar. Along with the exponential increase in R_H due to electron freeze-out, an abrupt change was observed in the slope of the R_H verus temperature curve over a narrow temperature range centered at about 100 K. A lack of thermodynamic equilibrium was also apparent from the time-constant effects observed about 100 K.

The high resistivity and lack of thermodynamic equilibrium below an abrupt process are characteristics similar to those reported for CdTe (Refs. 4 and 5) that had undergone various types of mechanical and electrical treatment. The CdTe results were explained using a compensation model which required shallow donors and an acceptor with one deep and one very deep level having a repulsive Coulomb barrier. Porowski and coworkers proposed a model for InSb requiring diffusion of impurity atoms between nonequivalent sites in the unit cell. Their model assigned different donor-electron ionization energies to the different sites in an attempt to explain the change in thermal electron freeze-out rates above and below 100 K. The time constants were assumed to be linked to the ion diffusion process between the sites.

In this paper we will describe additional measurements and a model which explains the pressure-dependent transport properties in high-purity InSb. Since the results for InSb are completely reversible with pressure, at least if one warms above ~ 100 K to reestablish equilibrium statistics, this material appears to provide a very useful vehicle for studying the compensation process.

Our model explains why undoped semiconductors of a given composition tend to be of a particular carrier type in spite of the fact that samples may be prepared in different laboratories by differing processes. The model also explains how highly compensated semiconductors (of either net carrier type) exhibit acceptor to donor ratios that seem fortuitously close to one. As was noted by Hilsum,[6] it would be necessary for N_A to be within less than 1% of N_D in some GaAs samples to obtain the observed compensation ratio. In the model to be presented it is seen that this condition is not in fact required even though it appears to be. Finally, the abrupt change in the Hall coefficient and the accompanying relaxation effects near 100 K are explained for pressurized InSb.

EXPERIMENTAL

The samples used in the measurements were approximately $0.5\times1.5\times1.5$ mm^3 and were cut from high-purity single-crystal ingots of InSb obtained from Cominco Limited. After cutting, the samples

were rinsed and etched for a few seconds in CP4A, prepared by mixing 14 ml of HNO_3 and 25 ml of CH_3COOH. The samples were then rinsed again and air dried. Electrical connections were made by soldering 0.003-in. platinum wires to the samples with indium containing 2 at. % tellurium. No *p-n* junction behavior was observed in any of the measurements.

Each sample was encapsulated in a Teflon capsule filled with a 1:1 mixture of isoamyl alcohol and *n* pentane, which acted as a pressure transmitting fluid. The encapsulated sample was then inserted into the bore of the inner cylinder of a self-stressing double-walled pressure vessel capable of pressures up to 30 kbar and discussed elsewhere.[7]

The pressures could be accurately applied to the samples at room temperature, 200 K, and 77 K. Estimates of differential contraction errors put a maximum uncertainty of ± 0.5 kbar on the pressures reported for all temperatures. The temperature was varied by mounting the pressure vessel on an Air Products closed-cycle helium refrigerator. Temperature was measured using a calibrated GaAs thermometer with associated electronics obtained from Lakeshore Cryogenics, Inc.

The Van der Pauw method was employed in taking the Hall measurements. All thermomagnetic effects except the Ettingshausen effect were eliminated by reversing current and magnetic field directions and taking appropriate averages. Since the Ettingshausen effect requires a temperature gradient and since a time interval of 10–30 min at a controlled temperature was allowed to elapse before final readings were taken, this effect was assumed to be negligible.

THEORY

Since the model considered here involves impurity states, we are concerned with the temperature range where the electron density is determined by extrinsic processes. At these temperatures there are less than 10^{20} electrons per cubic meter and the electron distribution in the conduction band is nondegenerate for temperatures above 20 K. We shall assume that there is a single donor and a single acceptor level, although it would be straightforward to extend the analysis to include more impurity levels.

The number of charge carriers at any given temperature can be determined from the charge neutrality condition:

$$p+N_D^+=n+N_A^- \tag{1}$$

for n conduction electrons, p holes, N_D^+ ionized donors, and N_A^- ionized acceptors in the sample. This can be written as an equation for the numbers of electrons or holes, but, since our samples are all n type we will consider electrons. For a sample containing N_D donors with degeneracy g_D and energy E_D below the conduction band and N_A acceptors with degeneracy g_A an energy E_A above the valence bands, Eq. (1) becomes, using the usual semiconductor statistics,

$$\frac{N_V N_C}{n}e^{-E_G/kT}+\frac{N_D}{(g_D n/N_C)e^{E_D/kT}+1} =n+\frac{N_A}{(g_A N_C/n)e^{(E_A-E_G)/kT}+1}, \tag{2}$$

where $N_C=2(m^*kT/2\pi h^2)^{3/2}$, k is Boltzmann's constant, T is absolute temperature, and m^* is the electron effective mass in the Γ conduction band. N_V is given by a similar expression where the electron mass is replaced by the average hole mass. The above equation is only correct if thermodynamic equilibrium can be achieved. Defining

$$\begin{aligned} a&=g_D^{-1}N_c e^{-E_D/kT},\\ b&=g_A N_C e^{-(E_G-E_A)/kT},\\ d^2&=N_C N_V e^{-E_G/kT}, \end{aligned} \tag{3}$$

Eq. (2) becomes

$$n^4+(N_A+a+b)n^3+(aN_A+ab-aN_D-d^2)n^2 -[abN_D+(a+b)d^2]n-abd^2=0 . \tag{4}$$

This equation can be solved numerically by any procedure for finding the roots of a polynomial. However, both for computational convenience and an insight into the physics of the process involved, it is useful to consider a series of approximations to Eq. (4).

In the extrinsic range where E_G is large, and hence d is small, the number of holes p can be neglected in the charge neutrality condition (although it is nonzero and influences the number of ionized acceptors). Thus

$$n^3+n^2(N_A+a+b)+n(N_A-N_D)a \approx(N_D-n)ab . \tag{5}$$

This describes a number of processes depending on the relative values of a,b and N_A in the coefficient

of n^2.

If E_D is small and hence a is the largest of the three, then

$$n(n+N_A-N_D)=(N_D-n)b \tag{6}$$

describes a process where, as temperature is lowered, an increasing number of electrons occupy acceptors levels which are an energy E_G-E_A below the conduction band. The n^3 term has been neglected in this expression since a is greater than $100n$ for these samples. Charge neutrality requires that $N_D^+=n+N_A^-$, and hence N_A^- cannot exceed N_D in spite of the fact that the process involves population by acceptor states. This is the case even if N_A is greater than N_D provided $E_A \gg E_D$. In this instance the material will be n type if the probability of reexcitation of the captured electrons to the conduction band is higher than that of capture by acceptors of additional electrons from the valence band. The donors are almost all ionized so that there are N_D-n negative acceptors and N_A-N_D+n neutral acceptors.

If E_G-E_A is large, then b is small and

$$n(N_A^-+n)\approx(N_D-N_A^--n)a \tag{7}$$

describes freeze-out of electrons onto the $N_D-N_A^-$ remaining uncompensated donors with decreasing temperature. Neglect of b fixes the number of negative acceptors at N_A, the total number of acceptors. Thus, in thermodynamic equilbrium, $N_A^-=N_A$ for small b. However, the important result to note is that Eq. (7) describes any process where the number of negative acceptors is fixed.

RESULTS AND ANALYSIS

The pressure derivative of the direct energy gap was observed to vary slightly with pressure being 15.5 ± 0.2 meV/kbar at $P=0$ kbar, 14.0 ± 0.2 meV/kbar at $P=8$ kbar, and 12.8 ± 0.1 meV/kbar at $P=14$ kbar, in agreement with the results of Gebbie and Smith.[8]

Figure 1 shows the variation of the Hall coefficient R_H with temperature. The decrease in carrier number and the abrupt change of slope at 100 K are clearly evident for pressures in excess of 8 kbar. These results confirm the data published in Refs. 1–3. Figure 2 is a log-log plot of mobility versus temperature. A downturn in the mobility for pressures in excess of 8 kbar accompanies the decrease in carrier number. These mobility results do not agree with those reported in Ref. 2 and are included here to show their general behavior.

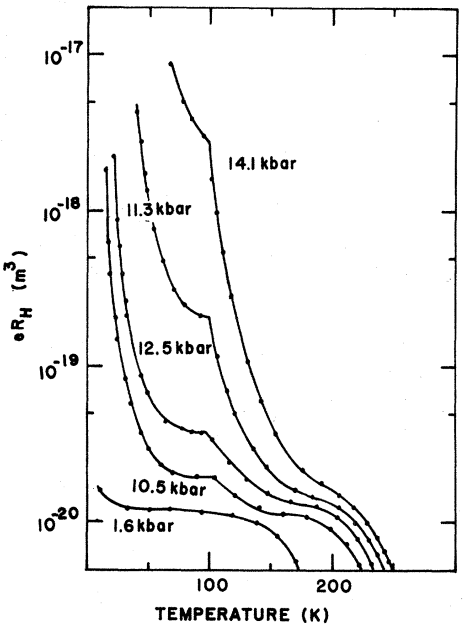

FIG. 1. Dependence of the Hall coefficient on temperature and pressure in a sample of InSb having an electron concentration of 9×10^{19} m^{-3} at $P=0$ and 77 K. The results are for the pressures (in kbars) indicated on the curves.

In Fig. 3 the logarithm of electron density is plotted versus $1000/T$ for several pressures. For pressures above 8 kbar, intrinsic processes were not seen below 170 K due to the increase in the band gap of InSb from 0.20 eV at ambient pressure to

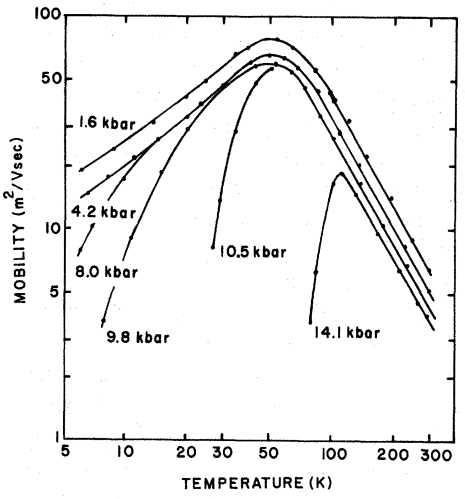

FIG. 2. Dependence of the Hall mobility on temperature and pressure for the pressures (in kbar) as indicated.

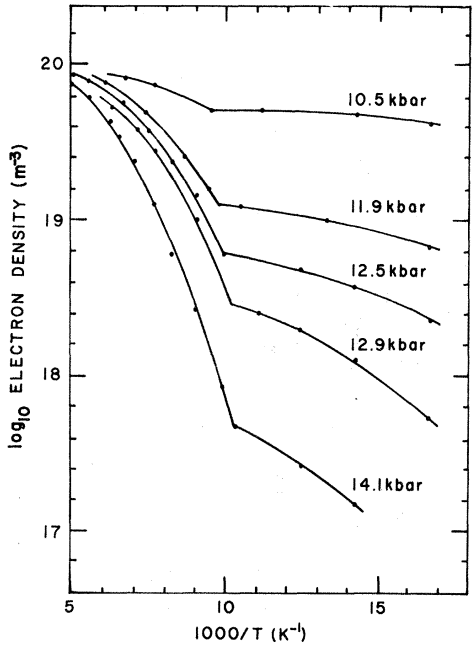

FIG. 3. Experimental (points) and calculated (lines) electron densities vs reciprocal temperature. The lines for temperatures above 100 K are drawn according to Eq. (6) while the lines below 100 K assume a lack of thermodynamic equilibrium and are drawn according to Eq. (7). The parameters used in all these theoretical fits were $N_D=9.0\times10^{19}$ m^{-3}, $N_A=1.75\times10^{20}$ m^{-3}, $g_D=2$, $g_A=4$, and $m^*(P)=0.014[E_G(P)/E_G(0)]$. The density of ionized acceptors N_A^- is assumed to be constant at its 100-K value for lower temperatures.

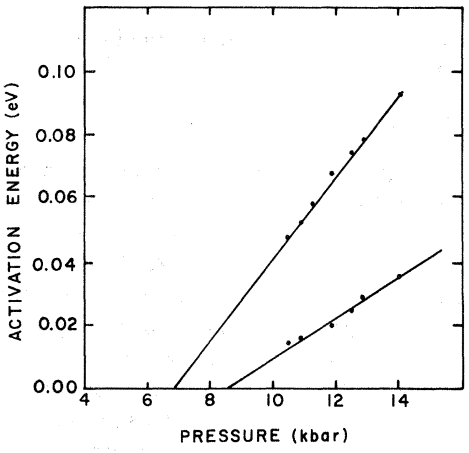

FIG. 4. Pressure dependence of the donor energy (E_D) and the energy (E_G-E_A) measured downward relative to the conduction-band minimum. The pressure derivatives are + 6 meV/kbar and + 13 meV/kbar, respectively.

0.32 eV at 8 kbar. The same sharp discontinuity in slope that was seen in the Hall coefficient graphs occurs at about 100 K. At first glance, one might expect such an abrupt change in a physical parameter to be due to a phase transition of some sort. On the other hand, we suggest that it is a logical consequence of nonequilibrium semiconductor statistics and it will be demonstrated that this interpretation is quantitatively consistent with the experimental results.

Consider first the high-temperature range of Fig. 3 with values of $1000/T$ between 5 and 10 K^{-1}. The curves are asymptoting to a donor number 9×10^{19} electrons/m^3 at all pressures where the process is one of redistribution of electrons between the conduction band and acceptor states. In this temperature regime equilibrium statistics apply and the slope of the $\log_{10}n$ vs $1000/T$ curve is determined by the energy E_G-E_A. The lines in the high-temperature range in Fig. 3 are drawn according to Eq. (6) for the values of N_D and N_A given in the figure caption where these impurity concentrations are assumed to be pressure independent. The electron effective mass is not an adjustable parameter since it scales with the pressure dependent gap $E_G(P)$. The fit in this high-temperature region is insensitive to E_D.

Figure 4 shows a plot of the E_G-E_A values that give the calculated lines in Fig. 3 versus pressure. The steeper slope was found to be 13 meV/kbar. Since E_G has an average pressure derivative of 13.4 meV/kbar in the pressure range between 8 and 14 kbar, it appears that E_A is almost pressure independent. This conclusion is supported by our own and published pressure results on doped p-type InSb.[9] For our samples the zero-pressure acceptor gap was found to be about 68 meV and the pressure derivative was slightly negative at about -1 meV/kbar. The published results just referred to were 120 meV and + 1 meV/kbar, respectively. The significance of these results is that the acceptor levels in InSb are quite deep, even in these doped cases, and their pressure derivatives are very small.

It is interesting to note that a change in g_A from 4 to 2 in the fits for Fig. 3 has little effect on the overall results. The pressure derivatives of the activation energies are unaffected. Only the intercept of the E_G-E_A curve is changed, being shifted to lower pressure by about 0.5 kbar. From Fig. 4 we estimate E_A to be about 0.32 ± 0.02 eV above the valence band at all pressures for the deep acceptors

in the undoped material.

The change of slope at about 100 K is not predicted by Eq. (4) and some modification of the analysis is required. The measured values of the Hall coefficient depend on the history of the sample for measurements taken below about 100 K. This metastability is associated with time constants which are longer than those of the apparatus.

The rate at which thermodynamic equilibrium is achieved in the sample can be described by a time constant τ that will depend on temperature exponentially through an expression of the form

$$\tau=\tau_0 e^{E_a/kT}, \tag{8}$$

where E_a is the activation energy. Dmowski[3] and co-workers studied the slow relaxation of the free-electron concentration in InSb. To induce the relaxation process, the pressure was always increased to 7.5 kbar or more and then the sample was cooled to 90 K before the pressure was reduced to the required value. For pressures less than 7.5 kbar they measured E_a given by Eq. (12) and found that it was pressure independent and equal to 0.30 ± 0.01 eV. They state that at higher pressures the situation is more complicated and the electron density is only exponential in time for small departures from equilibrium.

If this time constant results from the dissociation of neutral acceptors to form negative acceptors and holes, then both its numerical value and its pressure independence are explained. Also, it is evident from Fig. 4 that it would be necessary to raise the pressure to at least 7 kbar in order to produce an appreciable number of the negative acceptors, since these states are not in the gap at lower pressures. We therefore associate the activation energy E_a with the acceptor energy E_A.

A time constant with a large activation energy can account for quite a sudden slope change since, for an activation energy of 0.3 eV, the time constant increases by a factor of 24 when the temperature is reduced from 110 to 100 K and is increased by a further factor of 48 when the temperature is reduced to 90 K. For normal experimental procedures a point is reached when the time constant changes from seconds to hours and the number of negative acceptors appears "frozen in." Thus, the 0.3-eV activation energy for hole production appears to be responsible for the observed time-constant effects.

Equation (7) describes the situation when N_A^- is fixed as would be the case if the time constant were very long. The lines in the low-temperature range in Fig. 3 are drawn according to Eq. (7) where E_D was selected to give best fit in this low-temperature range. From Fig. 4 one obtains a pressure derivative $\partial E_D/\partial P=6$ meV/kbar. It seems probable that this donor level moves with the L conduction band since this is close to the calculated value of 8.3 meV/kbar for InSb and GaSb and even closer to the measured value of 5 meV/kbar for GaSb.[10]

DISCUSSION

The results of our analysis suggest a model with deep acceptor states tied to the valence band and donor states tied to the L conduction band. With increasing pressure the Γ conduction band moves away from the valence band, thus increasing the gap, while the L conduction band moves away from the valence band but with a smaller pressure derivative. The donor and acceptor levels, which are in the conduction band at zero pressure, move into the gap with increasing pressure as illustrated in Fig. 5.

At about 100 K the electronic properties of the samples become time dependent, and this can be interpreted in terms of a time constant for achievement of thermodynamic equilibrium that is long in comparison with the duration of the experiment. The rate of approach to equilibrium is unaffected by pressure and for InSb is described by an activation energy which is numerically equal to the acceptor energy E_A. We conclude, therefore, that the acceptor dissociation process $N_A^0 \rightarrow N_A^- + e^+$ is the predominant mechanism for the formation of negative acceptors.

This analysis is capable of explaining a number of apparently coincidental results in semiconduct-

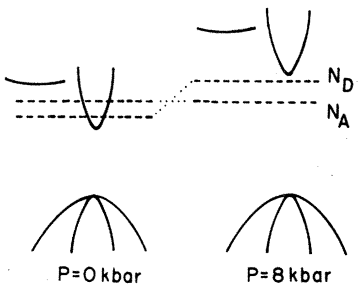

FIG. 5. Band structure of InSb at 0 and at about 8 kbar. The N_D donor states are assumed to be attached to the L conduction band and the N_A acceptor states are attached to the valence band.

ing materials. Many undoped semiconductors are n type and the ratio of acceptors to donors often appears fortuitously close to one. It would be necessary for N_A to be within less than 1% of N_D in some GaAs samples to obtain the observed compensation ratio.[6] Undoped InSb is always n type in spite of the fact that it is prepared in a number of different laboratories by differing procedures. In our model a material will always be n type if the donor energy is small in comparison to the acceptor energy irrespective of the relative numbers of donors and acceptors. At temperatures where the time constant for dissociation of acceptors becomes so long that their number is fixed, the material appears to have a compensation ratio very close to one. In some materials this could occur at or above room temperature in which case no anomaly would be observed in the Hall coefficient. The pressure independence of the time constant in InSb can be explained by the pressure independence of the acceptor level relative to the valence band.

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