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A nuclear relaxation study of hopping in p-type InSb

M Solanki-Moser, D P Tunstall and D M Finlayson
Department of Physics and Astronomy, University of St Andrews, St Andrews, UK

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Abstract. We present a low-temperature study of the charge and spin dynamics of holes, at density $\sim 10^{16}$ cm^{-3}, in the narrow-band semiconductor InSb. The conductivity and Hall coefficient are used to characterize the charge dynamics, and nuclear spin–lattice relaxation is used to monitor the electron spin dynamics. We have two samples; the first is cadmium-doped, p-type, uncompensated, of density 1.5×10^{16} cm^{-3} and the other is an initially identical sample, but additionally compensated by neutron transmutation doping to reduce the hole density to 7.2×10^{15} cm^{-3}. This dramatically increases the mobility in the hopping regime, by reducing correlation effects. An unusual nuclear relaxation rate enhancement at low field and at low temperatures is monitored for all three nuclei, ^{115}In, ^{121,123}Sb, over a wide field range; high field quenches the effect. We discuss possible nuclear relaxation mechanisms and speculate that the effect is due to electron spin fluctuations associated with the amorphous antiferromagnetic nature of the sample in which the effect is observed, which has a dopant density close to the critical density for the metal–non-metal transition.

1. Introduction

The metal–non-metal transition in InSb has been, over the years, a very active topic for n-type material. In contrast, there has been very little discussion of the transition in case of p-type doping. Similarly, just below the transition, review articles [1–3] on hopping appear to concentrate on electron hopping.

The juxtaposition of heavy- and light-hole bands, the reduced mobilities of holes as compared to electrons and the absence of spin characterization via electron spin resonance have conspired to complicate the model and to inhibit extended investigation in InSb.

The doping region which we target in this investigation is around 10^{16} cm^{-3}, p-type. n-type doping at this density in InSb is well above the Mott transition ($n_c \simeq 5\times10^{13}$ cm^{-3}), and the light holes are about 50% heavier than the conduction band electrons (0.021 m_0 compared to 0.014 m_0, where m_0 is the free-electron mass). If we can talk about hydrogenic acceptors in this context, then $a_B^h \simeq 0.67\, a_B^e$, where a_B^h, a_B^e represent Bohr orbital radii for the light hole and the electron respectively. This puts the critical doping density for the metal–non-metal transition due to overlapping light holes at 2×10^{14} cm^{-3}. In contrast the heavy holes have a mass 0.4 m_0; the Mott transition should occur at 1×10^{18} cm^{-3}. We reproduce in figure 1 a schematic of some trends in early data on p-type conductivity from Hofland and Honig (HH) [4], to which we return later in considering our NMR data. It is clear that at a doping density of 8×10^{16} cm^{-3}, InSb is metallic, and at 2×10^{16} cm^{-3} it is semiconducting. Experimentally therefore we assign the metal–non-metal transition to a density of 7×10^{16} cm^{-3}. The carriers at these

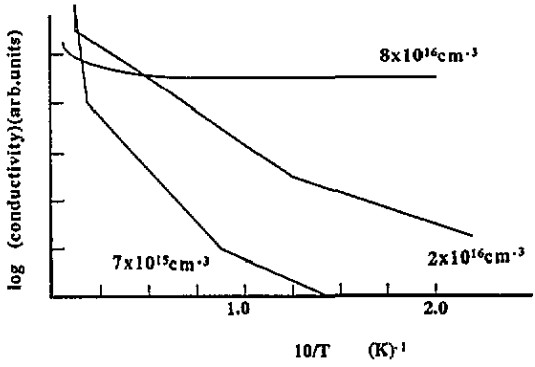

Figure 1. A schematic representation of the conductivity data of Hofland and Honig [4], in a plot against $1/T$. The high-density sample is clearly metallic, and the two lower-density samples show the two linear portions associated with ϵ_1 and ϵ_3 behaviour.

high dopant densities behave as if their mass is 0.13 m_0; this is close to the geometric mean of the heavy- and light-hole masses, 0.09 m_0.

The transport data in our sample (see later) characterizes our untreated sample as having a cadmium concentration of 1.5×10^{16} cm^{-3}, as measured by Hall effect. Our other sample, of acceptor density of 1.5×10^{16} cm^{-3}, treated with thermal neutrons to partially compensate the holes, has a net hole density of 7.2×10^{15} cm^{-3}. Both samples are therefore within an order of magnitude of the critical density for the metal–non-metal transition as measured experimentally. By comparison with the paradigm system in the metal–non-metal transition field, Si:P, our samples are in the strongly interacting regime, corresponding to an amorphous antiferromagnet.

We expect therefore the existence of low-lying excitations for both hole spin and charge, and our paper seeks to characterize these excitations using an array of transport techniques and NMR measurements.

The structure of the paper is that in section 2 we describe some earlier pertinent work in this area, in section 3 we detail the transport data taken on our samples, in section 4 the NMR data are described, and in section 5 we discuss the overall model that describes these data.

2. Previous work

The HH article [4] is the principal precursor to our study. Besides the transport data already described (figure 1), they carried out some NMR measurements. The focus of interest here was an anomalous helium-temperature behaviour of the spin–lattice relaxation rate of the ^{115}In nucleus in fields of up to 1 T. For doping concentration c such that 2×10^{15} cm^{-3} $< c <$ 2×10^{16} cm^{-3}, they discovered that the relaxation rate became larger as the sample cooled from 4.2 K towards 1 K.

In magnetic resonance such behaviour is highly unusual at helium temperatures. If the nuclear spins are relaxed by the fluctuations of the hole spins, then the fluctuation rate would have to be faster than the nuclear resonance frequency, and becoming slower as T is reduced from 4.2 to 1.5 K, in order to describe these data.

In their interpretation of the data, HH associated the requisite hole spin fluctuations with charge hopping. They supposed that the dominant relaxation mechanism for

the nuclear spins was generated by those pairs of hopping centres placed at just the correct distance apart such that the hopping frequency of the hole equalled the nuclear resonance frequency. Lowering the temperature was assumed to mean that more hole spins hopped at the relevant NMR frequency. At the lower temperature, the distance apart of the relevant hole spins would have to be smaller than at the higher temperature; the loss of hopping rate due to a lower temperature would then be compensated by a reduced distance separating the hole sites. The NMR data then indicated that there were more hole site pairs closer together. We reproduce in figure 2 a part of the relevant diagram of HH (their figure 3); the left-hand cross-hatched portion delineates the active fraction of pairs at 1 K, whilst the right-hand cross-hatched portion delineates the active fraction of pairs at 4 K.

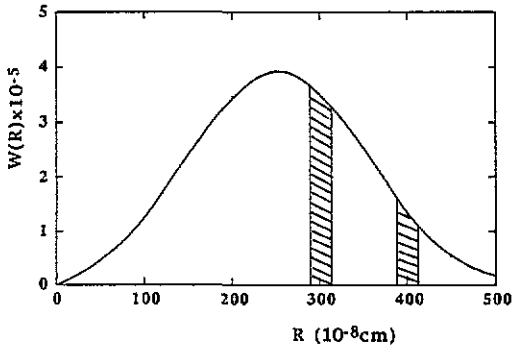

Figure 2. The probability W for nearest neighbours to be separated by R, drawn for a density of 10^{16} cm^{-3}. This is a redrawing of figure 3 of HH. The positions of the cross-hatched portions indicate the important pair separations for nuclear relaxation.

At about the same time, Jerome and Winter [5] published a study of ^{29}Si nuclear relaxation in Si:P. They used the hopping theory of Miller and Abrahams [6] in their interpretation. Their samples were predominantly n-type, with phosphorous, but compensated with boron. The total phosphorous density was 6×10^{16} cm^{-3}, substantially less than the critical concentration, $n_c = 4\times10^{18}$ cm^{-3}. It is therefore perhaps not surprising that the relaxation in this system was of standard behaviour, with T_1 longer at lower temperature. However a feature of [5] is the attempt to quantitatively develop the hopping theory of [6] and apply it to the NMR relaxation situation in doped semiconductors. They show (their figure 1) a probability distribution for hopping pairs as a function of energy separation Δ of the two sites, which is sharply peaked at $\Delta = 0$. The two sites between which the charge hops are assumed to differ in energy because of differing proximity of charged defects, present due to the compensation.

Thus $\Delta = 0$ means that the hops are between two sites at approximately the same distance from a static charged compensation centre. The hopping rate also depends on the distance R between the hopping centres in the pair, by a factor $\exp(-2R/a_B)$, where a_B is the Bohr orbital radius of the hole, and on temperature by a factor $\exp(-\Delta/k_BT)$. (For heavy holes in indium antimonide $a_B \sim 22$ Å and inter-site separations R can range from 10 Å up to 1000 Å, so that $\exp(-2R/a_B)$ can vary from ~ 0.5 to 10^{44}! The range of available hopping frequencies is enormous.) According to Jerome and Winter [5] the temperature variation of T_1 in their system is dominated by the 'efficient pairs of sites', those sites separated by $\Delta < k_BT$. There are more such sites at 4.2 K than at 1 K, so the T_1 at 4.2 K is shorter than at 1 K, a 'normal' hierarchy for T_1 against temperature. They support this conclusion with detailed numerical calculations.

HH [4] argue quantitatively that the efficient pairs of hopping centres are those where the $\exp(-2R/a_B)$ factor brings the hopping frequency into coincidence with the nuclear

Larmor frequency. Cooling the system from 4.2 K to 1 K slows the fluctuations down overall; this means that the new efficient pairs at lower temperature are those at smaller R, and, if there are more of them, then T_1 at 1 K will be smaller than at 4.2 K.

Hopping relaxation in n-type, uncompensated, InSb has been also addressed in an earlier paper [7]. In these experiments, metallic InSb was driven into the hopping regime by a large magnetic field, and in this region a large relaxation rate peak was observed at the same field for all three nuclei; the peak position as a function of field showed a large temperature dependence, e.g. 4 T at 1.5 K $\Rightarrow$ 8 T at 4.3 K. The coincidence of the peak position as a function of field for all three nuclei, in spite of their widely differing nuclear Larmor frequencies, is a clear indication that hopping at the nuclear Larmor frequency is not involved. We [7] tentatively assigned the peak to a tuning of the ESR frequency to a dominant hopping frequency in the sample. With hopping at the same frequency as the ESR frequency, then a low (nuclear resonance frequency) beat frequency will emerge which can relax the nuclear spins efficiently. In n-type InSb, hopping frequencies are very field dependent, so that variation of B changes both ESR and hopping frequencies.

3. Transport

The data from HH in figure 1 have already demonstrated the density of holes required to cause a metal–non-metal transition. We have undertaken transport measurements on the Cd-doped sample material with and without neutron-transmutation doping (NTD). This enables us to characterize rather precisely both N_A and N_D in the NTD sample on which the NMR measurements were taken.

From a plot of Hall coefficient against temperature, an extended range of temperature round 100–150 K exhibits a constant Hall coefficient. From these plateaux we deduce $p = 1.5\times10^{16}$ cm^{-3} in the untreated Cd-doped sample, and $p = 7.2\times10^{15}$ cm^{-3} in the NTD sample. This sample was irradiated for 33 min in Scottish Universities' Research Reactor at East Kilbride (in the small rabbit location). The known irradiation flux in this location in the reactor, and the irradiation time and cross-section for the nuclear reaction, are fully consistent with the measured densities. We conclude that $N_A = 1.5\times10^{16}$ cm^{-3} and $N_A - N_D = 7.2\times10^{15}$ cm^{-3}, from which we can deduce that the irradiation inserted an N_D of 7.8×10^{15} donors into the NTD sample. (The Hall coefficient calculations are based on $R = 1/ne$.)

In figure 3 the resistivity between about 1 K and 300 K for both the untreated and NTD samples is shown. As expected the introduction of the compensation centres by the NTD process has introduced new pathways for the hopping conduction at the lowest temperatures; even though the density of carriers is reduced by more than a factor of two during the NTD treatment, the conductivity is three to four times bigger at helium temperatures.

From the temperature dependence of the resistivity shown in figure 2, we can deduce a value of ϵ_1 ([8]) of about 5 meV in the temperature range 20–10 K, and a value of ϵ_3 of about 0.4 meV for both samples at $T < 10$ K. This latter region is the region where Miller and Abrahams' [6] theory is relevant; there is no evidence from our transport data of any variable-range hopping.

In both the uncompensated and the NTD sample, figure 3 demonstrates an absence of ϵ_2 processes in both samples. Whereas we expected this result for the NTD compensated sample, within the understanding that the presence of compensation centres diminishes the correlation effects on which the ϵ_2 process depends, its absence

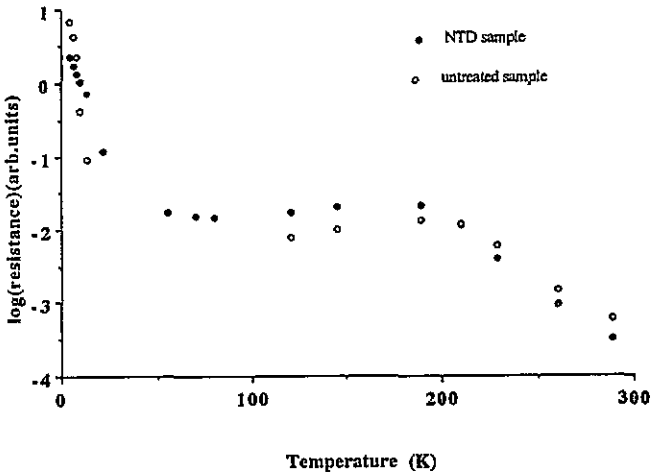

Figure 3. The resistivity of our two samples, as a function of temperature. When the same data are plotted as a function of $1/T$, then two regions of linearity appear below 20 K, again associated with ϵ_1 and ϵ_3.

in the uncompensated sample was a surprise. However, other workers (see, e.g. [9]) in work on p-InSb with varying compensation levels appear to find similar results. It may be that the degeneracy at the valence band edge promotes an absence of correlation effects. The value of $\epsilon_1 \simeq 5$ meV derived above is lower than the value quoted by Putley [10], 7.5 meV, for Cd, and we may suppose that our high doping levels broaden and shift an impurity band of p-type acceptors.

In conclusion of this section on the transport properties of our samples, we note:

(1) there is no evidence for variable-range hopping in the temperature range of our measurements;

(2) compensation, via NTD treatment, whilst reducing the number of carriers, greatly enhances low-temperature hopping, by providing vacant states adjacent to filled states for hole-hopping purposes;

(3) the critical density at the metal–non-metal transition appears to indicate that holes of effective mass 0.13 m_0 dominate the acceptor impurity band and its transport properties;

(4) our values of $\epsilon_1 \simeq 5$ meV and $\epsilon_3 \simeq 0.4$ meV indicate a broadened impurity band and low activation for nearest-neighbour hopping within the impurity band. In the helium temperature range, the ϵ_3 process controls the hopping.

4. NMR experiments

We present in figure 4 all our NMR spin–lattice relaxation data, on ^{115}In, on ^{121}Sb, and a couple of points on ^{123}Sb. These data were taken by field cycling techniques, where the NMR spectrometer operates at fixed frequency, but the magnetic field is switched to and from the field of interest where the relaxation proceeds. All these data refer to the NTD-treated sample.

Broadly the data reveal $T_1^{1.5K} < T_1^{4.2K}$ at low fields (up to ~60 MHz, ~6 T for ^{115}In and ^{121}b), but at 45 MHz for ^{123}Sb, $T_1^{4.2K} < T_1^{1.5K}$. However this latter frequency, for

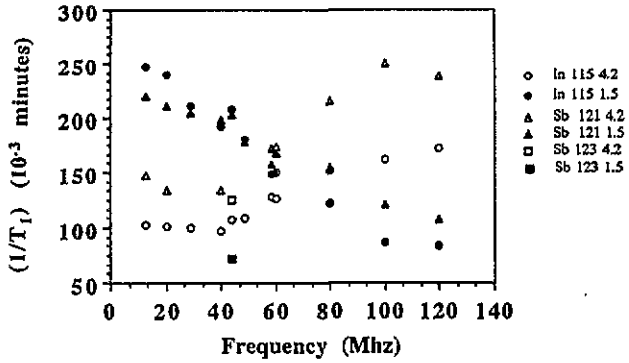

Figure 4. The relaxation rate for the three isotopes in the NTD sample, plotted as a function of the resonance frequency. The graph has data for two temperatures (4.2 K and 1.5 K). Note that the resonance frequency for the isotopes is approximately the same for ^{121}Sb and ^{115}In in the same magnetic field, but much lower for ^{123}Sb. Another way of saying this is that, at the same frequency, the resonance field is very different for ^{123}Sb.

^{123}Sb, corresponds to a field of 8 T, so that the entire data set is consistent with the idea that a field of 6 T is sufficient to quench the 'anomaly', where on cooling in the helium temperature range the spin–lattice relaxation become faster.

We compare these data initially with the data of HH [4]. Their experiments were restricted to fields of up to 1 T; we have extended the range up to 12.7 T and measured the different isotopes (their measurements were on ^{115}In alone). Immediately then we have confirmed the anomaly up to fields of about 6 T, and we have some indication that the anomaly disappears at approximately the same field no matter which nucleus is measured. For example, the cross-over field, where $T_1^{4.2K} = T_1^{1.5K}$, is 8 T for ^{115}In and 6 T for ^{121}Sb. The incomplete data set restricts any conclusion for the ^{123}Sb cross-over field to the statement that, if it exists, it is less than 8 T.

5. Discussion

In principle, then, our extended set of data could be taken to confirm the HH [4] qualitative analysis. In moving up to high field we have changed the separation R of the 'efficient' pairs from $R > R^*$ to $R < R^*$, where R^* is the most probable separation of pairs, corresponding to the peak of their figure 3. This attractive extrapolation of their ideas does not, however, withstand the more quantitative scrutiny made available from the theoretical treatment of [5] based on the nearest-neighbour hopping theory of [6].

First of all, the conductivity data appears to indicate that composite holes, with masses somewhere in between the masses of the heavy and light holes, dominate the hopping response. In our sample the most probable site separation R^* is 260 Å [4] and a hole radius (mass 0.13 m_0) is about 60 Å. The hopping rate, for an energy separation $\Delta \sim kT$, works out at about $1/\tau \simeq 10^9$. This places our experimental result, at frequencies $\omega \sim 10^8$ to 10^9 rad s^{-1}, in a regime where $\omega^2\tau^2 \simeq 1$ at the separation where the two impurity states between which the hopping occurs is equal to the most probable separation of acceptor centres. In such circumstances, where the 'efficient' pairs require a separation R such that $\omega\tau \simeq 1$, R must be $\sim R^*$ and cooling from 4.2 K to 1.5 K will have little effect on T_1. (This argument assumes, with HH [4], that the number of efficient hopping pairs is the dominant parameter.)

Besides the above, our application of the Jerome and Winter [5] equations appears to pose another problem for the HH [4] interpretation: the selection of 'efficient' hole-hopping pairs of states from the $(\tau/1 + \omega^2\tau^2)^{1/4}$ factor in the relaxation expression is not a sharp function. Although $\omega\tau \simeq 1$ is a condition providing that those pairs with hopping rate $1/\tau = \omega$ do give the largest contribution to the relaxation rate, calculations reveal that there is still a substantial contribution from, for example, pairs with $1/\tau \simeq \omega/100$ and those with $1/\tau \simeq 100\omega$ etc. (ω here is the nuclear resonance frequency.) The nuclear relaxation mechanisms does *not* select a narrow range of sites with a particular hopping separation. In the context of figure 3 of HH, our figure 2, this observation broadens the hatched areas; the observation in the previous paragraph pushes the hatched areas over to the left-hand side of the peak. Finally we point out that the hopping correlation rate, $1/\tau$, has a temperature dependence of $\exp(-\Delta/k_BT)$ in the temperature range of the NMR measurements, where conductivity values indicate that $\Delta \sim 0.4$ meV. A redrawing of figure 3 of HH would have to place the 1 K and 4 K lines at the top of the diagram much closer together; a change of temperature from 4 K to 1 K would need only a 60 Å shortening (not 100 Å, i.e. from 400 to 300 Å) of the separation of the relevant pairs to keep the hopping rate the same.

We have supported the above qualitative criticisms of the approach of HH [4] with detailed numerical calculations. We always find that the approach of [5] leads to a conventional temperature dependence for $1/T_1$ i.e. $(1/T_1)^{1.5K} < (1/T_1)^{4.2K}$. Perhaps the main point of issue is our deduction that the composite holes, of mass 0.13 m_0, dominate the charge fluctuations (and associated spin fluctuations) in this system. If this is correct, then the typical charge fluctuations at helium temperatures are similar to our NMR frequencies.

The comments above on [4] are of the interpretation of HH as applied via the theory of Jerome and Winter [5]; is there anything in our extended set of experimental data that also runs counter to their interpretation? We believe that the normal temperature dependence of ^{123}Sb (figure 4), at the same frequency where ^{115}In and ^{121}Sb show anomalous temperature dependence, is a clear indication that the mechanism responsible for the anomalous behaviour is not that adduced by HH [4]. If two nuclei exhibit the anomaly at a particular frequency, on the HH model the third nucleus present should also show anomalous behaviour. This observation is not totally convincing, however, since it would be possible to argue that the magnetic field needed to resonate ^{123}Sb nuclei at 45 MHz is sufficiently large to slow down the hopping frequencies. For example the cyclotron radius of a particle in a field of 8 T is $l = (h/eB)^{1/2} \simeq 100$ Å, and this, although larger than the hole radius, may be acting to reduce that radius.

We believe that there is sufficient doubt about the mechanism that produces the anomaly, on both theoretical and experimental grounds, that there is room for suggestions other than charge fluctuations via hopping. One such is that simple possibility, as indicated in the introduction, that we are here dealing with an amorphous antiferromagnet, with a range of hole spin excitations independent of the charge excitations that we have been discussing in the ideas dealing with hopping above. The possibility exists that such excitations are very fast, $1/\tau \gg \omega$. This will leave $1/T_1$ proportional to $(\tau/l + \omega^2\tau^2)^{1/4}$. Lowering the temperature causes a critical slowing down of these hole spin fluctuations and τ, the hole spin fluctuation dwell time, becomes larger as $T \Rightarrow 0$ [11, 12]. Hence $1/T_1$ increases. These antiferromagnetic spin fluctuations would be quenched by the application of a large magnetic field. Remembering that the anomalous temperature dependence of $1/T_1$ disappears at magnetic fields of about 6 T, and noting that the g factor for holes in InSb is -0.9 [13],

then an applied field of 6 T couples to the hole spins with an energy $\simeq k_B T$ for $T \simeq 4$ K. The Zeeman interaction becomes greater than kT in our temperature range, and effectively quenches the hole-spin flip-flops.

There is the possibility that data more extensive than that we have considered would reveal for example that the 1.5 K peak in relaxation at ~20–30 MHz for ^{115}In and ^{121}Sb was also present for ^{123}Sb at the appropriately lower frequency (~10–15 MHz); this would then link the observed effect more definitely to that already observed in the hopping regime in n-type InSb [7].

6. Conclusion

We have investigated more thoroughly the anomalous temperature dependence in nuclear spin–lattice relaxation first observed by HH [4]. We support the NMR measurements with detailed transport characterization of our NTD sample.

On both theoretical and experimental bases, we cast doubt on the simple analysis of HH [4]. We speculate that the origins of the effect may lie in the incipient amorphous antiferromagnetism of a metal–non-metal system just on the non-metallic side.

Acknowledgments

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