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Just-metallic germanium doped with arsenic: magnetic properties

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Abstract. We report results of an investigation into the magnetic properties of the electron spins in a sample of germanium heavily doped with arsenic; the doping process is effected by the neutron transmutation technique, on germanium isotopically enriched to 95% ^{74}Ge. The process leaves the sample with 9% compensation, and with a true random distribution of donor spins. Temperatures down to 40 mK and uniaxial stresses up to 0.36 GPa are utilized, and the integrated electron spin resonance is used to monitor the magnetic properties. Electrical characterization of the sample at ambient stress shows hopping behaviour, placing the density of the sample below the critical density for the metal–non-metal transition at this pressure. Electron spin resonance (esr) in the dilution refrigerator is only observed with stress applied; this minimal stress drives the sample metallic. A large 'stress- tuning'effect is inferred. The data on the electron spin susceptibility in the just-metallic sample, as monitored by the integrated area of the esr line at the lowest stress, shows at most only a small variation with temperature; a small broadening as T is lowered appears to be matched by a similar decrease of intensity. Further, $\langle 110 \rangle$ uniaxial stress enhances the intensity of the esr line. The sharp contrast with Si:P is discussed. We speculate that the experiment is detecting only the spins in the strongly metallic portions of the sample.

1. Introduction

The metal–non-metal transition in silicon doped with phosphorus, and in germanium doped with either antimony or arsenic, has been extensively studied [1]. Both silicon and germanium are systems which exhibit the anomalous scaling exponent $\nu = 1/2$, when the zero-temperature extrapolation of the conductivity $\sigma(0)$ is expressed as a function of $(n - n_c)^\nu$, where n is the donor density and n_c is the critical donor density at which the metal–non-metal transition occurs [2–4].

On the just-metallic side of the transition the electron gas in uncompensated Si:P is strongly correlated, as evidenced by the change in sign of the $T^{0.5}$ temperature dependent correction to the conductivity, both as n tends to n_c, and as the magnetic field is varied [2]. The absence of negative magnetoresistance, the strong temperature dependence of the magnetic susceptibility, and the anomalous critical exponent in the zero-temperature conductivity as n tends to n_c are all thought to be extra symptoms of strong correlation [2–4]. There is considerable current controversy about the correct interpretation of the electrical results in this area [5–7], and indeed about the results themselves.

To explore this region of unusual properties close to the metal–non-metal transition we have undertaken electron spin resonance (esr) measurements, similar to those [8] in Si:P,

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in a low-compensation Ge:As sample ($n_c = 3.5 \times 10^{17}$ cm^{-3}), with a view to establishing whether the magnetic properties exhibited at high density in Si:P are comparable to those in a system of interacting delocalized electrons an order of magnitude lower in density. Stress is applied to the sample to 'stress-tune' the critical concentration (n_c); the conditions are such that, although our sample at ambient stress has a concentration of donors lying below the critical concentration, and is thus insulating, we only report here our experiments where the stress is sufficiently high to drive n_c below the concentration of donors. Thus all data reported are on metallic germanium.

In the next section we discuss the electrical characterization of the sample used. We go on to set out our esr results, including the effects of uniaxial stress and temperature variation on the magnetic properties, and finish with a discussion of these results, particularly in comparison to the Si:P data [8].

2. Electrical and stress characterization

Homogeneous doping with controlled disorder in germanium is difficult. There is a substantial body of evidence for clustering of impurities, and other non-random distributions of dopant in the host matrix [9, 10]. For this reason we have used neutron transmutation doping of isotopically enriched germanium to introduce arsenic donors. The starting material before neutron transmutation had electrical properties that indicated that the dopant concentration before irradiation was $\sim 10^{13}$–10^{14} cm^{-3}. The conditions of irradiation, and the isotopic purity of the starting material, were such that for the sample on which we have undertaken stress measurements, Ge22, the expected donor concentration (compensation ratio) was 2.83 (0.09). Here the first number refers to the concentration in units of 10^{17} cm^{-3} and the number in brackets to the ratio of the number of doped acceptors to donors (N_A/N_D). The small compensation comes about because of the residual ^{70}Ge in the starting material, before irradiation. After irradiation each sample was subjected to an annealing treatment lasting 100 h at 430 °C. This thermal treatment has been demonstrated as necessary to eliminate both stress due to As doping, and damage by fast-neutron irradiation [11].

Table 1. The Hall densities at 300 and 77 K for the two samples.

	^{77}n ($\times 10^{17}$ cm^{-3})	^{300}n ($\times 10^{17}$ cm^{3})
Ge22	1.93	3.25
Ge24	1.77	2.92

After irradiation and annealing some electrical measurements were made on the samples to establish their donor concentration. A crude parameter in determining donor concentration is room-temperature resistivity [12]; Ge22 has a value of 16 mΩ cm, which translates via the graphs in [12] to a density of 3.0×10^{17} cm^{-3}. Table 1 lists the values of the carrier density obtained for two samples from the Hall coefficients R at 300 and 77 K, using $R = 1/ne$ (we assume that the Hall factor is unity). In the literature the value of R at 300 K is usually taken as the better indicator of density in germanium systems [13, 14]. Figure 1 shows low-temperature resistivity data for Ge22, taken at ambient stress, confirming hopping behaviour at the lowest temperatures (0.5 K), and thus indicating both proximity to the metal–non-metal transition and that this sample is definitely on the insulating side of that transition at ambient stress.

One further point on the electrical characterization of the samples. A good indicator

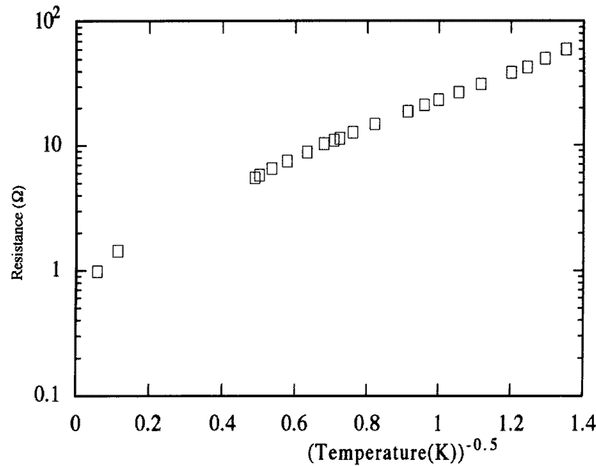

Figure 1. A semi-logarithmic plot of the electrical resistance of Ge22 against $T^{-0.5}$, showing hopping at the lowest temperatures. A straight line could be drawn through the lowest-temperature data.

of the metallicity of a sample is the lack of temperature dependence of the resistivity in the range 4.2–1.2 K. Good metals have resistivities $\rho_{1.2} \sim \rho_{4.2}$, whilst semiconductors have $\rho_{1.2} \gg \rho_{4.2}$. The ratio $X = \rho_{1.2}/\rho_{4.2}$ is a sensitive indicator of the transition, and a value of $X = 1.4$ is thought to mark the dividing line [14] between metal and non-metal; samples with X less than this are metals, samples with greater X are insulators. Ge22 has a ratio X of 3.4, indicating that this sample lies just on the insulating side of the transition.

We checked whether this ratio is consistent with the measured Hall concentration in the following manner. From figure 7 of [15] (a study of resistivity as a function of temperature of germanium samples doped n-type from the melt) it is possible to measure values of X for several different concentrations at ambient stress (a small extrapolation to 1.2 K is needed since the data only go down to about 1.35 K). For example a Hall concentration of 2.5×10^{17} cm^{-3} leads to an X value of about 11 000, and a Hall concentration of 2.8×10^{17} cm^{-3} to an X value of about 100. By connecting up such data points with a smooth curve it is possible to make a prediction for the Hall concentration to be associated with particular X values; the concentration associated with an X value of 3.4 turns out to be 3.3×10^{17} cm^{-3}. Thus X for Ge22 is consistent with the Hall effect densities. We conclude then that n/n_c in Ge22 is 0.93 ± 0.06 at ambient stress. This ratio is based on a value of n of $(3.25 \pm 0.10) \times 10^{17}$ cm^{-3} and on a value of n_c of $(3.5 \pm 0.2) \times 10^{17}$ cm^{-3}.

We address next the question of the effect of stress on our samples. The configuration we have used involves $\langle 110 \rangle$ stress up to 0.36 GPa on the Ge22 sample. This particular stress orientation favours two of the conduction band minima over the other two in germanium (there are four such minima, along the four $\langle 111 \rangle$ directions in k-space). The stress then increases the anisotropy of the donor wave-functions, and expands them [16]. Electrical experiments with $\langle 111 \rangle$ stress on Ge:As [17], a stress orientation that favours one minimum over the other three, and therefore makes the anisotropy even more marked, have established that, for insulating samples, a stressed sample is closer to the metal–non-metal transition than the unstressed sample. For example, if we take figure 7 of [17], the sample As-5, density 2.82×10^{17} cm^{-3}, is clearly an insulator at ambient stress (curve labelled As-5(0)), whereas under a stress of 0.15–0.2 GPa along $\langle 111 \rangle$ it is almost metallic, with a resistance ratio

$X = \rho_{1.2}/\rho_{4.2}$ of approximately 1.6. In the same figure 7 of [17], another curve, labelled As-6(0), has a very similar low-temperature dependence of its resistivity; this curve, taken at ambient stress, refers to sample As-6, of density 3.61×10^{17} cm^{-3}. This confirms the critical density in Ge:As at ambient stress as about 3.5×10^{17} cm^{-3} and indicates that $\langle 111 \rangle$ stress of 0.15–0.2 GPa pushes this critical density down to approximately 2.8×10^{17} cm^{-3}. Further confirmation of the critical density [18] and of the effect of $\langle 111 \rangle$ stress [19] is available.

However, our experiment is concerned with $\langle 110 \rangle$ stress. As compared to $\langle 111 \rangle$ stress, $\langle 110 \rangle$ stress moves two valleys down and two valleys up. A semi-quantitative argument as to the relative efficacies of $\langle 110 \rangle$ and $\langle 111 \rangle$ stress in shifting the critical density of the metal–non-metal transition, i.e. stress-tuning, would first note that $\langle 110 \rangle$ stress produces less anisotropy in the real space wavefunction. However, $\langle 110 \rangle$ stress lies at 35° to two of the $\langle 111 \rangle$ axes of a cube, and at right angles to the other two. The components of stress along the two axes are only 0.82 of the applied stress. Thus, for a given amount of stress, the $\langle 110 \rangle$ direction compared to the $\langle 111 \rangle$ direction produces marginally less wavefunction expansion, but also less wavefunction anisotropy (n_c is pushed down by wavefunction expansion and up by wavefunction anisotropy). Lacking at this stage any direct measurements of resistivity under stress on our samples, we therefore assume that $\langle 110 \rangle$ and $\langle 111 \rangle$ stresses are equal in their 'stress-tuning' effect on n_c. Further justification for this assumption is obtained by the comparison between the effects of stresses in these two directions on the resistances of metallic samples of Ge:Sb [21]. Thus at 0.15–0.2 GPa, we estimate that Ge22 has a value of $n/n_c = 1.16$. If we further assume that at these densities the effect of stress in tuning n_c is linear, then at 0.36 GPa, our highest stress, $n/n_c \sim 1.55$. With a linear connection between n_c and pressure, and taking the phrase 'between 0.15 and 0.2 GPa' [17] to mean 0.175 GPa, we deduce the relation between critical concentration n_c and $\langle 110 \rangle$ stress P as

$$n_c = -4.0P + 3.5$$

where the units of n_c are 10^{17} cm^{-3} and those of P are gigapascals.

Given that the data below are taken at stresses between 0.12 and 0.36 GPa, all these experiments are on metallic samples, $1.08 < n/n_c < 1.55$. We estimate an error bar on these figures such that the first figure should read 1.08 ± 0.05, whilst the second should read 1.55 ± 0.25.

The compensation ratio K in our samples can be calculated from the degree of isotopic enrichment of the starting material to be 0.09; this follows from the neutron transmutation doping process and the 95% isotopic enrichment in ^{74}Ge of the starting material [20].

The sample was formed into an approximately 15 mm × 1 mm × 1 mm single-crystal bar, with the pressure anvils acting on the 1 mm × 1 mm faces and with the rf coil of length 6 mm wound around the centre of the bar. Homogeneity of stress is assured in such a configuration. The orientation was $\langle 110 \rangle$ along the axis, and the Zeeman magnetic field was applied in a direction perpendicular to the $\langle 110 \rangle$ axis of the crystal bar. The absence of any shifts in the resonance position with applied stress indicates that the magnetic field lies close to the $\langle 100 \rangle$ axis [22]. This experimental configuration applies to all the experiments in this article.

3. Results

We first observed the esr at 4.2 K for the Ge24 sample at zero stress in a high-Q spectrometer. The width of the Ge:As resonance was 1.6 G, taken at a Zeeman spectrometer frequency of 15.7 MHz, and the g value was 1.55 ± 0.02. In another 4.2 K experiment, on

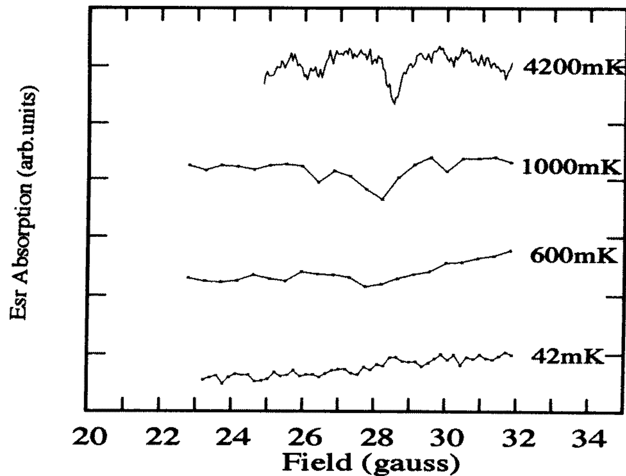

Figure 2. The esr spectra at 63 MHz at four representative temperatures and with an applied $\langle 110 \rangle$ stress of 0.12 GPa. Note that esr absorption is represented by a negative-going peak. Clearly the line at 28.3 G is best defined at the highest temperatures and it broadens and weakens as the temperature is lowered.

Ge22 at 63.2 MHz with 75 MPa of uniaxial $\langle 110 \rangle$ stress applied, a g value of 1.57 ± 0.04 was obtained. The intensities of the signals, compared to those from a sample [8] of Si:P of density $\sim 3 \times 10^{18}$ cm^{-3}, were fully consistent with the relative numbers of spins in the samples.

The rest of the data were taken with the sample mounted in the dilution refrigerator, with its integral stress cell. Here the Q of the spectrometer is reduced, because, for reasons associated with thermal conductivity and the need to minimize heat loss, coaxial cable of low Q has to be used in the tuned circuits. We present selected data taken at intermediate and high stress, from 0.12 to 0.36 GPa, when the sample is in its metallic state. Figures 2–4 show the data: although the signal to noise ratio is poor, some general trends can be established. Figure 2 shows the evolution with lowering temperature of the esr signal at a stress of 0.12 GPa. The signal is very narrow at 4.2 K, about 0.5 G, but broadens and loses intensity as the temperature decreases to 600 mK; by 42 mK it has completely disappeared. Figure 3 shows the behaviour of the esr absorption, for a different but overlapping temperature range, at a stress of 0.36 GPa. The signal at the higher stress is much better defined at low temperature, but again the same general trends are observed, of broadening and weakening as the temperature is lowered. Finally in figure 4 the effect at 300 mK of increasing stress on the esr signal is highlighted: again the signal is much better defined at the higher stress. The reason for the increased definition appears to lie in an increased intensity as the stress increases, rather than in any narrowing of the line. Since the line is so remarkably narrow at 4.2 K at low stress it is clear that the observed effects in figure 4 are not connected with the removal of stress inhomogeneity by the application of stress, an effect that has been observed to increase the intensity in other situations in the esr of semiconductors [22].

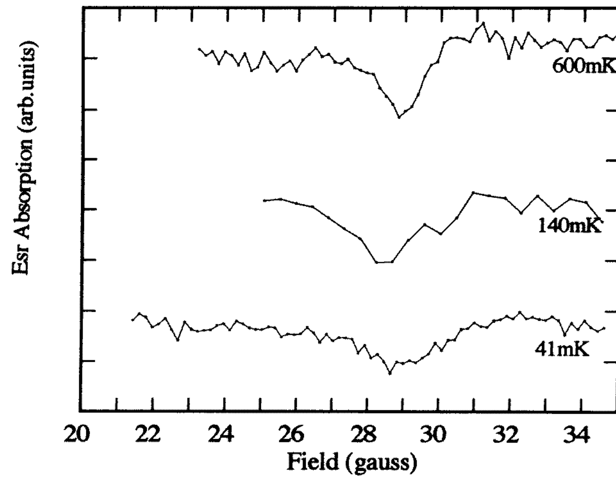

Figure 3. The esr spectra at 63 MHz at three representative temperatures and with an applied ⟨110⟩ stress of 0.36 GPa. Again, as in figure 2, the line broadens and weakens as the temperature decreases.

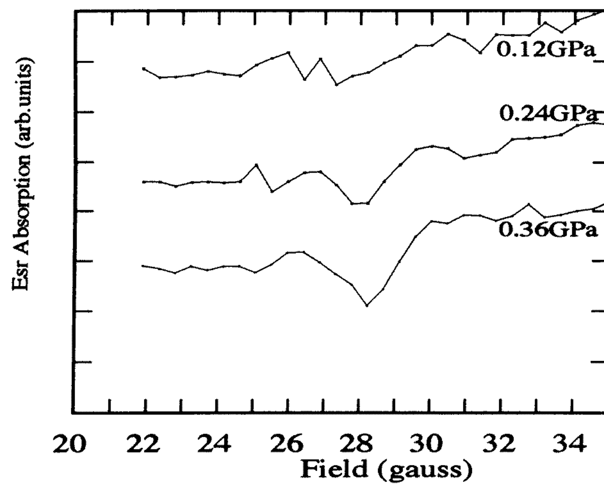

Figure 4. The esr spectra at 63 MHz and 300 mK, for three values of ⟨110⟩ stress. Hardly any resonance can be observed at the lowest stress, but with increasing stress the line is slowly revealed.

4. Discussion

The measured g values at zero and low stress in our ultra-low-field experiments at 4.2 K in Ge24 and in Ge22 agree with earlier, more accurate, values [9, 23, 24].

Figure 2 shows the 0.12 GPa data, exhibiting a signal that broadens and weakens as the temperature is lowered: at 600 mK the signal has disappeared. (Remember that as the temperature drops the Boltzmann factor in the population of the spin levels leads to a $1/T$ dependence for the integrated signal intensity, for non-interacting, localized,

spins. For metallic electron spins, by contrast, we expect a temperature independent susceptibility.) Given the poor signal to noise it is difficult to say much about the integrated esr intensity, which is proportional to the electron spin susceptibility [25]. However, the broadening, accompanied by a loss of intensity, is consistent with an approximately temperature independent spin susceptibility. We can be more certain about the similar but rather better data at 0.36 GPa, shown in figure 3. Here we can say that, over the temperature range 600–40 mK, the susceptibility does not vary by more than 30%. Clearly the low-temperature signal intensity is enhanced by stress, and this permits the tracking of the signal down to lower temperatures at the highest stress.

A temperature independent susceptibility at $n/n_c = 1.08$ would be a surprise; our Si:P measurements [8] and observation by others [9, 26] on both insulating and metallic samples indicate that a move across from insulator to metal does not change the temperature dependence of the electron spin properties very greatly. For example, the temperature dependence [26] of the susceptibility at $n = 1.09n_c$ and at $1.25n_c$ is still considerable in this temperature range; between 4.2 K and 40 mK the susceptibility rises by a factor of 300% in the $n = 1.25n_c$ sample and by more than 1000% in the $n = 1.09n_c$ sample. It is perhaps less surprising to find χ temperature independent at 0.36 GPa in our germanium sample; here $n/n_c \sim 1.55$, rather deeply metallic. A further unusual feature is the clear indication from figure 4 that stress enhances the susceptibility; more usual behaviour is that, since stress expands the donor wavefunction and thus pushes the system towards a more metallic state, and towards stronger exchange interaction, then the susceptibility falls. These germanium data contrast with our data on Si:P [8], covering the density range $0.86n_c$ to $0.93n_c$. There, the esr line broadens by a factor of 12 as the temperature falls from 4.2 K to 30 mK, and a stress of 0.24 GPa narrows the line by about 20% at the lowest temperature. Both these effects occur with the esr intensity remaining constant.

Exchange (J) effects are rather different in Ge-based and Si-based systems, as has been discussed by Matsunaga and Ootuka [14]. Their conclusion is that, for identical n/n_c, J is about 0.8 times as large in Si as in Ge. However, on the just-metallic side, this slightly stronger exchange in the dilute system coexists with the reduced energy scale that goes with the germanium system. Features such as impurity-band widths are presumably much smaller in the dilute system at the same $n/n_c > 1$, and yet the exchange is predicted to be larger. There is therefore some basis in theory for predicting differences between the magnetic properties of the just-metallic electron gas in the germanium and silicon systems.

Another suggestion as an explanation of both the temperature independence of the susceptibility and the enhancement of the susceptibility by stress in the Ge data is that the esr signal being observed originates from metallic islands or portions, which are extended by the wave function expansion generated by stress.

The esr from the quasi-localized spins that still exist in the metallic state [26, 27] in Si:P and which account for the temperature dependence of the spin susceptibility are not observed in NTD Ge:As esr experiments. Possibly the enhanced exchange in germanium prevents this localized behaviour in the metallic region. However, the observed weak temperature dependence of the spin susceptibility does not seem to be consistent with the large variations exhibited in susceptibility measurements [14] in Ge:Sb unless two different sorts of spin are being observed in the two sets of experiments. It seems possible that the spins that produce the large temperature dependence in the susceptibility might also be the spins with large hyperfine interactions leading to large and unobservable widths. The neutron transmutation doping of the germanium samples may be an important consideration here: the definitively random nature of the doping process may preclude these quasi-localized spins.

One further consideration should be kept in mind: these NTD samples do have a small

residual concentration of acceptors, there because of the imperfect isotopic purity of the pre-radiation material. 9% compensation is not large, but there is evidence [28] that such small compensation can change the electrical conductivity scaling away from a power law with $\nu = 1/2$ towards one with $\nu = 1$. In moving away from the half-filled impurity band via this residual compensation, one must also worry about changes in magnetic properties. There has been theoretical debate, and some experimental evidence, in this area [29–30]. The evidence from our work, where the sample impurity band is slightly off half-full because of the residual compensation, and the susceptibility is temperature independent, might be taken to support the theoretical work of Milovanovic *et al* [28].

The evidence in figures 2–4 indicates that stress slightly narrows the esr linewidth, as well as substantially increasing the esr intensity. This narrowing effect is rather similar to that observed [8] in Si:P and is an anticipated feature of stress experiments, since stress reduces the hyperfine interaction as well as making the system more metallic.

5. Conclusion

In a highly doped sample of germanium, with $n \sim 0.93n_c$ at ambient stress, esr signals have been obtained at low temperature, down to 40 mK. A large 'stress-tuning' effect is available in this material. The sample is stressed in order to lower n_c such that the density range of the measurements is $1.08 < n/n_c < 1.55$. At $n = 1.08n_c$ the spin susceptibility may be temperature independent. At $n = 1.55n_c$ this temperature independence is more certainly confirmed. Furthermore stress enhances the spin susceptibility.

This latter effect may arise because of the enhanced exchange. Another possibility is that stress enlarges the metallic region of the sample, bringing more spins into the measurement frame and thus increasing the signal. This existence of metallic regions would also provide a natural explanation of the temperature independence of the susceptibility. The sharp contrast with extensive data in Si:P may be primarily caused by the definitively random nature of the donor atoms in our samples, since they were doped by the neutron transmutation technique. The comparison between the two systems may be vitiated by the residual small compensation present in the germanium samples.

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