diffraction maxima at large angles of 2θ. It is possible that during the preparation of the "strained" samples and their treatment afterwards, a certain amount of phase I was introduced but this was felt to have negligible influence on the basis of the previous experiment.[18]

The lowering of the transition temperature with removal of strain is consistent with general behavior of all *B*1-type compounds.[19,20] If the transition temperature of 2.2°K can be associated with a completely strain-free sample then the critical magnetic field extrapolated to zero of about 800 G appears rather high and places InTe(II) as a candidate for type-II superconductivity. Further experiments are planned to investigate this. On the basis of an "average" valency, InTe(II) obeys the Matthias rules. In further comparison with compounds of the same structure, InTe(II) is the eleventh superconductor in the number of *B*1-type compounds reported as of 1 January 1963[20] and extends the range of reported transition temperatures from 5.6–17.8°K to 2.2–17.8°K.

[18] Recently, Geller *et al.* [S. Geller, A. Jayardman, and G. W. Hull, Jr., Appl. Phys. Letters 4, 35 (1964)] published results on the transition temperature of InTe(II) as a function of the stoichiometric ratio of In to Te. For a ratio of one-to-one they get a transition temperature of 3.2–3.45°K which is close to the value of Banus *et al.* We have no explanation of this except for strain since we prepared our samples very carefully and our measured lattice constants agree with those of Geller *et al.* within 0.02 Å for a ratio of one-to-one.

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Negative Magnetoresistance in Impurity Conduction

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Negative magnetoresistance is observed at 4.2°K in Cd-doped *p*-type GaAs, vapor deposited *n*-type GaAs, and P-doped *n*-type Ge. In *n*-type GaAs prepared by Czochralski or horizontal-Bridgman techniques, samples with carrier concentrations less than about 10^{16} show negative magnetoresistance at 4.2°K which goes through a maximum at fields less than 10 000 G and becomes positive at high fields. At concentrations greater than 10^{16} there is no clear indication of a maximum at fields up to 20 000 G. The ratio of longitudinal to transverse magnetoresistance in the impurity conduction range is a function of temperature and field, but at 1.4°K it exceeds 0.9 both for negative magnetoresistance at low fields and for positive magnetoresistance at high fields. The over-all trends of the data on GaAs and other materials require two competing processes to account for the magnetoresistive behavior. One of these is the effect of the magnetic field in reducing orbital overlap which has been demonstrated by Sladek and Keyes on *n*-Ge and *n*-InSb. A competing process which could operate in the "hopping" region of impurity conduction might be an increase in the population of a set of states of higher energy and mobility than the ground states due to a reduction in the energy separation between them.

INTRODUCTION

NEGATIVE magnetoresistance has been reported in *n*- and *p*-type InSb,[1–3] Ge doped with As,[4] Sb,[5] and Cu,[6] *n*-type GaAs,[7,8] B-doped Si,[9] and P-doped Si.[10] We report here the observation of negative magnetoresistance in Cd-doped GaAs, P-doped Ge, and

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TABLE I. Sample characteristics.

Sample	Growth direction	300°K ρ (Ω-cm)	300°K R (cm³/C)	77°K ρ (Ω-cm)	77°K R (cm³/C)	4.2°K ρ (Ω-cm)	4.2°K R (cm³/C)	1.4°K ρ (Ω-cm)	1.4°K R (cm³/C)
1	110	0.022	100	0.017	126	0.041	108		
2a	111	0.052	310	0.040	420	0.205	330	0.22	330
2b	111	0.063	440	0.047	600	0.41	450	0.47	540
3	horizontal Bridgman	0.066	420	0.041	570	0.39	460	0.48	490
4	111	0.17	910	0.15	1500	5.2	1340		
5	111	0.20	1430	0.427	2720	24	2280	86	
			1220	0.169	2050		1320		
			930		1350				
6a	110	0.245	866	1.14	1430	87.5	1200	275	···
		0.342	1200	2.09	2010	91.0	1100		···
			1250		1750		···		···
6b	110	0.50	2520	15.1	16800	2.8×10^4	···		···
		0.54	2560	12.6	10900		···		
			2540		10700		···		

n-type GaAs. The results on n-GaAs agree with and supplement those of Nasledov *et al.*[7,8,11]

EXPERIMENTAL DETAIL

The measurements reported in this paper were all performed on samples having three pairs of Hall probes (also used for resistivity measurements) positioned at the ends of sidearms projecting from the body of the sample. The samples are 8×1 mm and between 0.7 and 1 mm thick. The sidearms are about 0.4 mm wide and 2.0 mm apart. All measurements reported here were made on etched samples.

The measurements were dc potentiometric except for the samples in which magnetoresistance was small. In these cases the zero magnetic-field signal was bucked out and the unbalance produced by the magnetic field was amplified with a Keithley 150 electronic voltmeter and displayed on a Brown strip-chart recorder. The signal was symmetrical for both current directions.

Sample homogeneity was checked by measuring three Hall coefficients and two resistivities. In the samples of lower resistivity Hall coefficient variations of less than 5% could be obtained. However, at resistivities greater than 0.1 Ω cm, such uniformity has not been obtainable.

EXPERIMENTAL RESULTS ON n-GaAs

Crystals of n-GaAs were measured with carrier concentrations ranging from 2×10^{15} to 3×10^{18}. Above 10^{18} no magnetoresistance was observed within our detection limits (~0.02%). Most samples were pulled from either quartz or AlN crucibles, but several horizontal-Bridgman-grown samples and one vapor-grown sample were included. The method of growth had no apparent effect on the results.

In Table I are shown the resistivity and Hall coefficient (at 4000 G) at 300, 77, 4.2, and 1.4°K for the set of samples which have been used for Figs. 1–6. For three samples which showed considerable inhomogeneity all three values of Hall coefficient are given. One important feature on this table is the resistivity increase from 4.2 to 1.4°K. Since all of these samples exhibit negative magnetoresistance, this behavior is in contrast to that of n-Ge, in which negative magnetoresistance occurs only in samples for which the resistance is constant or decreases between 4.2 and 1.4°K.[12]

Figure 1 shows the variation of magnetoresistance with magnetic field at 4.2°K for a number of crystals of differing electron concentrations. The principal features are similar to those reported on other materials. Referring to the data in Table I, it may be seen that (a) at a fixed field strength the effect has a maximum at some carrier density as in n-Ge,[5] (b) at low fields the negative magnetoresistance increases approximately linearly with H as in[2] p-InSb and p-Ge,[6] and (c) the samples of

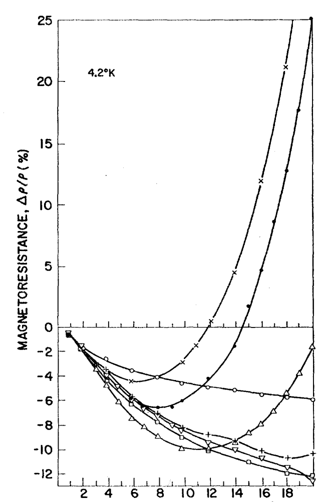

FIG. 1. Magnetoresistance versus magnetic field at 4.2°K for n-GaAs crystals listed in Table I: ○–1, ▽–2a, □–2b, +–3, ●–5, △–6a, ×–6b.

[11] D. N. Nasledov and O. V. Emel'ianenko, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (Institute of Physics and the Physical Society, London, 1962), p. 163.

[12] W. Sasaki and R. Debruyn Ouboter, Physica **27**, 877 (1961).

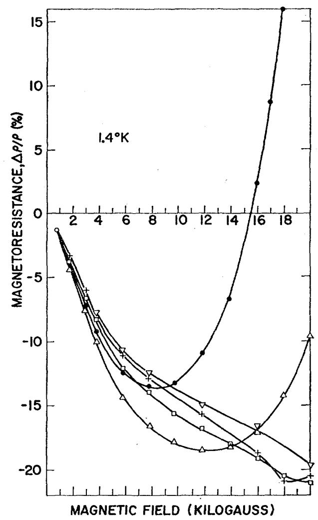

FIG. 2. Magnetoresistance versus magnetic field at 1.4°K for n-GaAs crystals listed in Table I: ▽–2a, □–2b, +–3, ●–5, △–6a.

In Figs. 4 and 5 are shown the dependence of magnetoresistance on the angle between current direction and magnetic field for two samples. Sample 2b (Fig. 4) is a pulled crystal and sample 3 (Fig. 5) is a horizontal Bridgman-grown sample. The current is in the plane normal to the growth direction for both crystals. Both show an approximate $\sin^2\theta$ dependence at 77°K as is expected for spherical energy surfaces. The small longitudinal magnetoresistance is probably due to fringing of the current in the vicinity of the Hall probes. In the impurity-conduction region the longitudinal and transverse values of negative magnetoresistance are comparable. At 1.4°K and 3.8 kG the variation with θ is less than 10% in both samples. In higher resistivity crystals, which have observable resistivity gradients, the magnetoresistance at 77°K deviates markedly from a $\sin^2\theta$ dependence. For example, the longitudinal magnetoresistance of sample 5 at 77°K is 40% of the transverse value. However, the negative magnetoresistance at

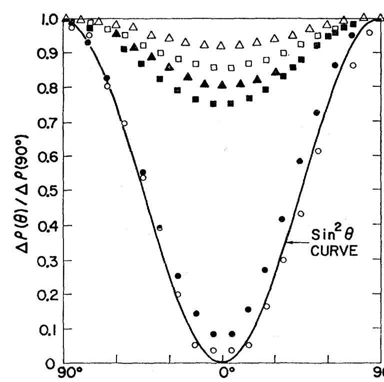

FIG. 4. Magnetoresistance versus angle between magnetic field and current direction for pulled n-GaAs. ○–77°K, □–4.2°K, △–1.4°K; open symbols 3.8 kG, filled symbols 20 kG. Crystal 2b of Table I.

lower concentration show a reversal from negative to positive magnetoresistance as the field increases as in[3] p-InSb and n-Ge.[5,13] Figure 2 shows similar data at 1.4°K. The magnitude of the negative magnetoresistance is greater at the lower temperature, and the sign reversal moves to higher values of H.

The crystals which show a sign reversal of magnetoresistance as H is increased are inhomogeneous as can be seen from Table I. However, the same sort of behavior is observed in p-InSb and n-Ge where it is apparently not associated with impurity gradients. Figure 3 shows the temperature dependence of Hall coefficient and magnetoresistance for two crystals (4 and 5) of about 6×10^{15} electron concentration. The Hall effect maximum is fairly sharp at this doping level and the close coincidence between it and the onset of negative magnetoresistance is clear.

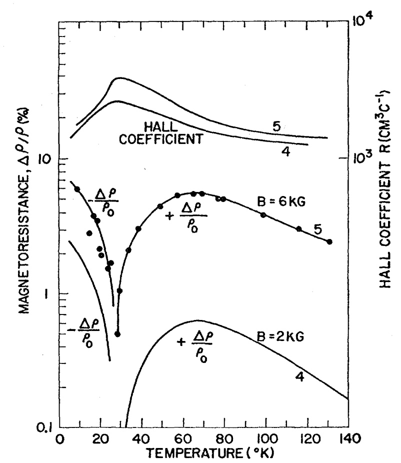

FIG. 3. Magnetoresistance and Hall coefficient versus temperature for n-GaAs of about 6×10^{15} electrons per cm³. Crystals 4 and 5 of Table I.

[13] Y. Furukawa, J. Phys. Soc. Japan **17**, 630 (1962).

1.4°K and 4000 G is almost independent of θ, varying only 3%. At the same temperature at 20 000 G, the magnetoresistance is positive but again relatively independent of θ since it varies only 7%. The longitudinal values are less than the transverse for both positive and negative magnetoresistance.

Figure 6 is a plot of negative magnetoresistance versus carrier concentration which includes our results and those of Nasledov.[8] The general agreement is seen to be reasonable. The limit on the low carrier-density end is still to be determined due to the nonavailability of suitable material.

Cd-DOPED GaAs

Negative magnetoresistance has also been observed in three Cd-doped p-GaAs samples. One sample (a) was pulled from quartz and has a donor background of the order of 10^{17} per cm³. The other two samples were from a crystal pulled from alumina (b and c) and have a donor background of the order of 10^{16} cm^{-3}. The hole concentrations (at room temperature), of the three samples are, respectively, 10^{17}, 3×10^{17}, and 2.7×10^{17}. Thus the compensation (N_D/N_A) is probably about 50% in sample a and less than 10% in samples b and c, while the impurity concentrations are probably nearly equal. Figure 7 shows the resistivity and Hall effect (at 4000 G) as a function of temperature for these three samples and Fig. 8 shows the magnetoresistance at 77 and 4.2°K as a function of magnetic field.

The normal magnetoresistance (positive) at 77°K is equal for all three samples within experimental error (about 10%), and is proportional to H^2 both at room temperature and at 77°K. The negative magnetoresistance at 4.2°K is different for the three samples. For a it has a maximum of 0.8% at 10^4 G, for c, a maximum of 0.2% at about 8000 G, and for b maximum of 0.1% at about 8000 G. The magnitudes of the negative magnetoresistance are small, but they are comparable to the positive magnetoresistance value at 77°K which reaches 1% only at 20 kG. The resistivities of these samples increase with decreasing temperature at 4.2°K and there are no measureable Hall coefficients below 20°K. The activation energy of resistivity between 12 and 40°K for a is 1.5×10^{-3} eV and for b is 1.9×10^{-3} eV (the other has not been measured).

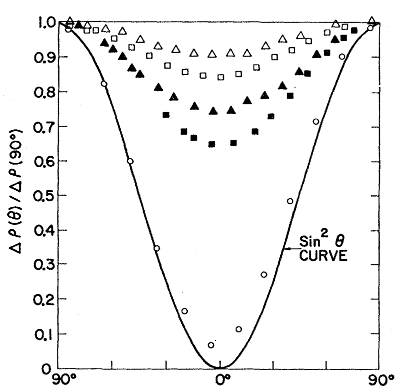

FIG. 5. Magnetoresistance versus angle between magnetic field and current direction horizontal-Bridgman grown n-GaAs. ○–77°K, □–4.2°K, △–1.4°K; open symbols 3.8 kG, filled symbols 20 kG. Crystal 3 of Table I.

PHOSPHORUS-DOPED Ge

Only a few observations were made on P-doped Ge. In one sample ($n=5\times10^{16}$ cm^{-3} at 300°K) magnetoresistance was positive only. In a 3×10^{17} cm^{-3} sample negative magnetoresistance was observed at 1.4°K with 4000 G; but at 20 000 G the magnetoresistance was positive, and it was positive for all fields at 4.2°K. An 8×10^{17} cm^{-3} sample showed negative magnetoresistance at 4.2°K which had the same order of magnitude as As-doped Ge reported by Sasaki *et al.*[5]

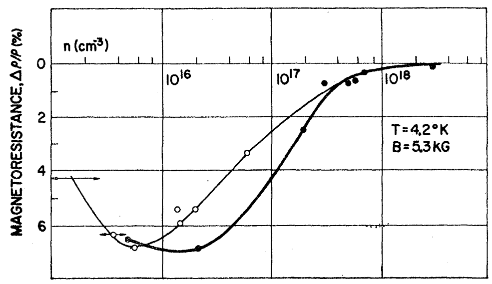

FIG. 6. Magnetoresistance of n-GaAs at 4.2°K and 5.3 kG versus room-temperature carrier concentration. The heavy line is Nasledov's data (Ref. 8); the light line is ours.

DISCUSSION

Figure 9 is a summary of the materials and doping ranges in which negative magnetoresistance has been observed. The various observations all occur in the impurity-conduction range of dopings and among the various materials all ranges of impurity conduction are represented.[14,15] In the impurity-band range negative magnetoresistance is observed in n-Ge (Sb, As, P), n-Si(P), and n-GaAs (Si,Te); in the transition range in n-GaAs (Si) and p-InSb; and in the hopping range in p-Si(B), p-Ge(Cu), and p-GaAs(Cd).

The characteristics of negative magnetoresistance in

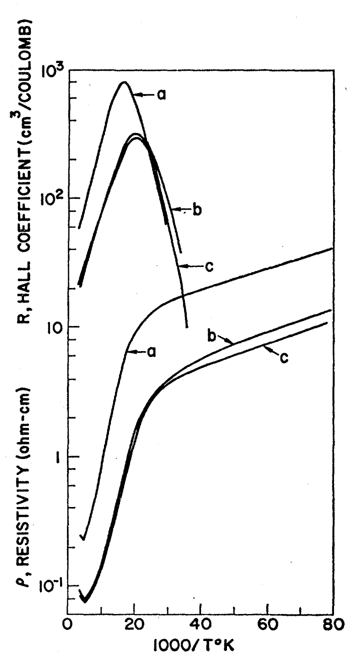

FIG. 7. Hall effect and resistivity versus $10^3/T$ for p-type GaAs (Cd-doped). Sample a is about 50% compensated, b and c less than 10%.

[14] Two types of impurity conduction are well established and are designated by the terms "hopping" and "impurity-band." In Sb-doped Ge, for example, "hopping" conduction occurs at dopings between approximately 9×10^{14} and 2×10^{16} cm^{-3} while "impurity-band" conduction occurs at dopings between approximately 2×10^{17} and 4×10^{18}. Between 2×10^{16} and 2×10^{17} there is a "transition" range. These ranges can be observed in the data of Fritzsche (Ref. 15).

[15] H. Fritzsche, J. Phys. Chem. Solids 6, 69 (1958).

the various materials are similar, as far as they have been reported. Longitudinal magnetoresistance is somewhat less than transverse, but the dependence is not strong [*n*-Ge,[12] *p*-InSb,[3] *p*-Si,[9] *n*-GaAs (Figs. 5 and 6)]. This is also observed in positive magnetoresistance in the impurity conduction range (*n*-Ge[16] and *n*-GaAs). Field dependence of negative magnetoresistance shows an approximately linear increase with H at low fields and a saturation at higher fields for heavily doped samples (*n*-Ge, *n*-GaAs, *p*-Si, *p*-Ge). In samples of lighter doping it passes through a maximum and decreases, turning positive at highest fields (*n*-Ge, *n*-GaAs, *p*-InSb, *p*-GaAs). Negative magnetoresistance increases with decreasing temperature whether the resistivity increases or decreases.

There seem to be only two possible kinds of mechanisms which could account for negative magnetoresistance: Either the magnetic field increases the mobility or "hopping" probability of the carriers, or the magnetic field causes a redistribution of carriers among energy states of differing mobility. These are not necessarily mutually exclusive.

The localized spin model proposed by Toyozawa,[17] in which the scattering produced by the localized spins is reduced by the effect of the magnetic field in aligning the spins, is the only model of a mobility-increase mechanism which has been put forward, and it cannot account for negative magnetoresistance in the "hopping" or "transition" ranges.

It has been shown[18,19] that the magnetic field reduces the mobility or "hopping" probability in the hopping region by reducing orbital overlap. In view of this effect it seems necessary to postulate a model involving sets of energy states of differing mobilities in order to account for negative magnetoresistance, at least in the absence of impurity-band conduction. The general character of the magnetoresistance observations is consonant with a two-energy-state model of impurity conduction[20,21] in which the energy difference between the two states (or sets of states) is reduced by the application of a magnetic field thus increasing the occupation of higher energy states which have a higher mobility than the ground states due to greater orbital overlap.[22] Since the magnetic field also restricts the orbitals, thus reducing overlap, the resistance change may be either an increase or decrease depending on the relative magnitude of the two effects. For this reason negative magnetoresistance would not invariably occur in the impurity-conduction region.

A two-state model would, in general, predict a variation of Hall effect with magnetic field. However, since the Hall effect has so far been unmeasureable in the "hopping" region, the prediction cannot be verified there. In the impurity-band region in *n*-GaAs we have not found any significant variation of Hall coefficient with magnetic field, in agreement with Nasledov and Emel'ianenko.[7,11] However, Sasaki and Kanai[4] have reported a Hall-effect variation correlated to negative magnetoresistance in *n*-Ge, so the failure to observe a Hall-effect variation in *n*-GaAs cannot by itself exclude the applicability of this sort of model to impurity-band conduction.

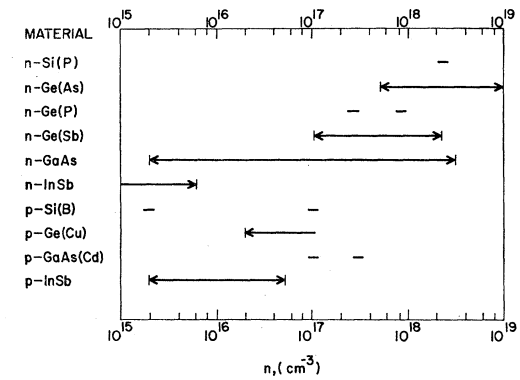

FIG. 9. Range of carrier concentration in which negative magnetoresistance has been observed for various semiconductors.

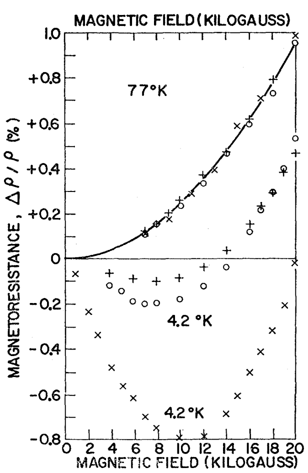

FIG. 8. Magnetoresistance versus magnetic field at 77 and 4.2°K for *p*-type GaAs (Cd-doped). ×–sample a of Fig. 7, +–sample b, ○–sample c.

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