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Magnetoresistance measurements in the bulk amorphous Ge_xSe_{1-x} system

R. M. MEHRA, HEMANT KUMAR, S. C. AGARWAL, SURINDER KOUL, P. C. MATHUR
Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India

Magnetoresistance (MR) measurements were made on bulk amorphous Ge_xSe_{1-x} samples in the temperature range 80 to 300 K and magnetic field up to 8 k G (0.8 T). It is found that MR is negative at all temperatures. At a given temperature, the magnitude of the negative MR and the exponent n of magnetic field variation are found to increase with an increase in the proportion of selenium. These results have been analysed in terms of various existing models of MR.

1. Introduction

There appears to be widespread agreement that the study of magnetoresistance (MR) in the case of amorphous semiconductors provides an insight into the origin of conduction, along with the degree of localization and mobility distribution in localized states. MR was first observed in heavily doped *n*-germanium by Sasaki and Ouboter [1]. Since then MR has been observed in a number of semiconductors [2–10]. Most amorphous semiconductors usually exhibit both positive and negative MR. Negative MR is independent of the angle between the direction of the magnetic field and the sample current. Unlike crystalline semiconductors, MR in the case of amorphous semiconductors is highly sensitive to annealing. The variation of MR with magnetic field in amorphous semiconductors is quite different from that in heavily doped crystalline semiconductors. The study of MR in amorphous semiconductors has mostly been made on *a*-germanium and silicon films [11–13]. The main reason for this is that these monoatomic materials from the simplest amorphous system showing generally one type of disorder, namely that of atomic position. Furthermore, their crystalline counterparts are well understood in terms of the interpretation of data for their amorphous counterparts.

Mell and Stuke [11–13] in their MR measurements on *a*-germanium films found the MR to be negative over a wide range of temperature and magnetic field; a positive component of MR was, however, observed at low temperatures and magnetic fields. Clark *et al.* [14] also found almost the same behaviour of MR, except for an absence of positive component of MR at temperatures as low as 77 K and magnetic fields as low as 100 G (1 G = 10^{-4} T), although in both the experiments the films of *a*-germanium were prepared by an electron-beam evaporation technique using different substrates. Detailed measurements of MR were subsequently made on *a*-germanium films [15] on annealed samples (annealing temperature 670 K). The MR was again negative over a wide range of temperatures. However, the magnitude of the MR was found to increase with decrease of temperature. A small positive component was also observed at about 170 K. Thus there is general agreement among various workers that in *a*-germanium films negative MR increases, due to annealing at high temperatures. This observation is against the Mott and Davis [16] model of negative MR, in which its origin is considered to be due to the interaction of localized spins with the electrons in the localized states. The model of Movaghar and Schweitzer [17], however, explained the observed effect of annealing to some extent. The temperature and magnetic field variation of the MR may agree with the predictions of the exchanged interaction model of Khosla and Fischer [2]. Several more investigations [18, 19] have been carried out in amorphous semiconductors;

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TABLE I Composition analysis of bulk amorphous samples of Ge_xSe_{1-x} at two arbitrary locations on the surface of the samples

Sample number	Initial composition (at %)		Actual composition (at %)			
			Location I		Location II	
	Ge	Se	Ge	Se	Ge	Se
1	10	90	12.45	87.55	12.02	87.98
2	20	80	21.76	78.24	20.97	79.03
3	30	70	28.16	71.84	28.49	71.51
4	40	60	39.01	60.99	39.82	60.18
5	50	50	48.83	51.17	49.32	50.68
6	60	40	59.27	40.73	60.05	39.95
7	70	30	68.39	31.61	69.17	30.83

nevertheless the experimental facts reveal the difficulty of explaining the MR data satisfactorily.

In the present work, results of MR measurements on bulk amorphous samples of the Ge_xSe_{1-x} system are reported. This system is of particular interest because of the scarcity of MR data on bulk samples comprising elements from two distinctly different groups, namely tetrahedrally-bounded amorphous semiconductors (germanium) and the chalcogens (selenium). The measurements were taken at temperatures 80, 200 and 300 K. It is found that MR is negative and that the exponent n of magnetic field variation (see Section 3) increases with an increase in the concentration of selenium in germanium, and with the ambient temperature. The observed results have been interpreted in terms of various existing models of MR.

2. Experimental details

Bulk amorphous samples of the Ge_xSe_{1-x} system ($x = 0.7$, 0.6, 0.5, 0.4, 0.3, 0.2 and 0.1) were prepared by the quenching technique described previously [20]. The homogeneity and actual composition of the samples were determined by scanning electron microscopic and X-ray studies (Philips SEM-505 with EDAX). The results so obtained are given in Table I. X-ray diffraction traces of all seven samples at 300 K are shown in our earlier paper [21]. The absence of sharp structural peaks in the X-ray diffraction traces confirmed the amorphous nature of the samples. The crystallite size t of various samples was calculated by using the relation [22]

$$t = \frac{51\lambda}{\beta \cos\theta} \qquad (1)$$

where λ is the wavelength of X-rays used and is 0.154 051 nm in the present experiments. β represents the half-width of the broad structural peak and θ is the angle of diffraction. The crystallite size is found to range from 2 to 2.6 nm, which also indicates that samples are amorphous in nature. Aluminium electrodes were evaporated on to the entire area of opposite faces of the samples. Samples were placed in a non-magnetic cell (which provides proper shielding) in a sandwich configuration. For measuring MR, change of current through a standard resistance was measured with the help of a Keithley nanovoltmeter. The voltage across the standard resistance was offset before applying the magnetic field. Observations were taken by reversing the direction of the magnetic field and of the sample current. The value of MR was found to be independent of the angle between the current and the direction of the magnetic field.

3. Results and discussion

The variation of MR with magnetic field B for bulk amorphous samples $Ge_{70}Se_{30}$, $Ge_{60}Se_{40}$, $Ge_{50}Se_{50}$, $Ge_{40}Se_{60}$, $Ge_{30}Se_{70}$, $Ge_{20}Se_{80}$ and $Ge_{10}Se_{90}$ at ambient temperatures 300, 200 and 80 K is shown in Figs. 1, 2 and 3 respectively. At all temperatures the conductivity increases with increase of magnetic field, indicating that MR is negative for magnetic fields up to 8 kG (the maximum field used in the present investigation). For both germanium-rich ($Ge_{70}Se_{30}$, $Ge_{60}Se_{40}$ and $Ge_{50}Se_{50}$) and selenium-rich samples ($Ge_{40}Se_{60}$, $Ge_{30}Se_{70}$, $Ge_{20}Se_{80}$ and $Ge_{10}Se_{90}$), MR decreases with increase in ambient temperature and increases with the proportion of selenium. However, it can be observed from these figures that the negative MR for germanium-rich samples at low temperatures (80 and 200 K) increases with magnetic field but saturates at high temperatures (300 K), and then starts decreasing with further increase in magnetic field. Unlike

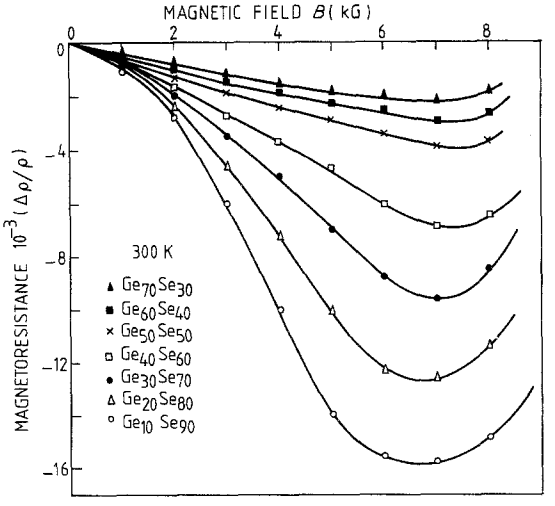

Figure 1 Plot of magnetoresistance ($\Delta\rho/\rho$) against magnetic field (B) for amorphous samples of Ge_xSe_{1-x} at ambient temperature 300 K.

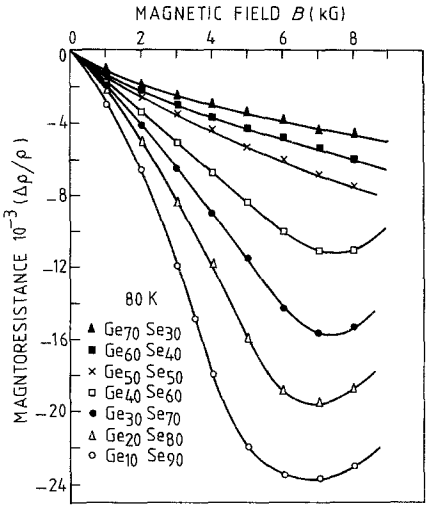

Figure 3 Plot of magnetoresistance ($\Delta\rho/\rho$) against magnetic field (B) for amorphous samples of Ge_xSe_{1-x} at ambient temperature 80 K.

germanium-rich samples, the MR in selenium-rich samples increases continuously with increase of magnetic field, and decreases with further increase of magnetic field. For all these samples, the negative MR at low magnetic fields is found to satisfy the relation

$$-\Delta\rho/\rho \propto B^n \qquad (2)$$

where $\Delta\rho$ represents the change in the resistivity with the application of magnetic field (B) and ρ is the resistivity in the absence of magnetic field.

The study of the variation of MR and exponent n with temperature and composition is of great importance from the point of view of examining the suitability of a particular model for a particular situation. Therefore MR data at low magnetic fields (~ 5 kG) have been replotted as $\ln(\Delta\rho/\rho)$ against $\ln B$ for all ambient temperatures. The values of n calculated with the help of these plots for different compositions and ambient temperatures are shown in Table II. It can be observed from Table II that for germanium-rich samples the value of n is less than unity, whereas for selenium-rich samples it is greater than unity. It is also obvious from the table that n is a function of temperature and sample composition. It may be mentioned here that measurements of d.c. conductivity [21] on these samples revealed that conduction in germanium-rich samples at low temperatures is characterized by Mott's variable-range hopping (VRH) [16] in the localized states near the Fermi level (E_F), and in the high temperature region the conduction takes place in localized states near the band edges. On the other

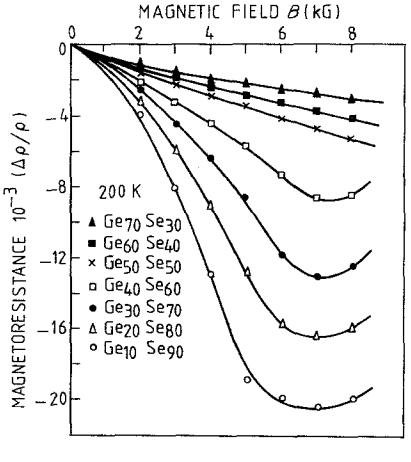

Figure 2 Plot of magnetoresistance ($\Delta\rho/\rho$) against magnetic field (B) for amorphous samples of Ge_xSe_{1-x} at ambient temperature 200 K.

TABLE II Values of exponent n of the variation of MR with magnetic field, for amorphous samples of Ge_xSe_{1-x}

Sample number	Sample composition		n		
	Ge	Se	80 K	200 K	300 K
1	70	30	0.56	0.68	0.71
2	60	40	0.69	0.78	0.82
3	50	50	0.79	0.86	0.91
4	40	60	0.97	1.03	1.12
5	30	70	1.12	1.29	1.35
6	20	80	1.26	1.45	1.58
7	10	90	1.54	1.70	1.85

hand, the conduction in selenium-rich samples is due to thermally assisted tunnelling of charge carriers in localized states at band edges throughout the temperature range.

The present results have been analysed in terms of various existing models of MR, namely the localized spin moments model [23], the two-band model [24] and the semiclassical random-walk hopping model [17]. Toyozawa [25] has explained negative MR in heavily doped semiconductors on the basis of second-order exchanged scattering between the extended-state electrons and localized magnetic states of the electrons in the impurity atoms. Khosla and Fischer [8] included third-order terms to obtain better quantitative agreement with the experimental results. However, this localized spin moments model could not explain the observed increase of negative MR with increasing annealing temperature. Another discrepancy in this model was that the value of the spectroscopic g factor calculated from the negative component of MR for the localized spin orbital is found to be 1000, which is very high. The present results for germanium-rich samples can qualitatively be well explained with the help of Movaghar and Schweitzer's (M–S) semiclassical random-walk hopping model [17] in the temperature region where the conduction takes place, and by Mott's VRH [16] and by the two-band model [24] when conduction is of the thermally activated type.

According to the M–S model the defect states near E_F are spread out in energy, with singly occupied states lying below E_F, doubly occupied states lying above E_F, and empty states distributed randomly. The hopping transport occurs by (a) hopping from a doubly occupied state to an empty state (normal hop); (b) an upward hop from a singly occupied state with either a simultaneous spin flip (anomalous hop) or without a spin flip (normal hop); and (c) a downward hop with a nonsimultaneous spin flip (anomalous hop), or without a spin flip (normal hop). The source of MR is the magnetic-field dependence of the spin–lattice relaxation time for anomalous hops. Hopping time for the normal hops is independent of magnetic field. The inclusion of g shift (which is the difference between the g values of localized and free electrons) in the magnetic-field dependence of the average internal field gives rise to the negative component of MR. The internal field component, being independent of the g shift, gives the positive component of MR.

The negative component can be expressed as

$$\frac{\Delta R}{R} = \frac{P_a[T_{1(2)}(H_0) - T_{1(2)}(0)]}{(1-P_a)\nu_0^{-1}\exp[(T_0/T)^{1/4}] + P_a T_{1(2)}(0)} \quad (3)$$

where the quantity P_a depends upon the number of sites with an internal degree of freedom, the temperature, and the probability of finding an alternative route to avoid the anomalous process. $T_{1(2)}(H_0)$ denotes the averaged spin–lattice or spin–spin relaxation time as a function of magnetic field, whichever is the fastest. ν_0 is the hopping frequency, and T_0/T is the ratio of characteristic disorder energy to the thermal energy [26].

It was shown in d.c. conductivity measurements [21] that the value of T_0 increases with the increase of selenium concentration in germanium. The increase in negative MR with the increase of selenium content is understood by considering the above increase in T_0 and Equation 3. From this equation it is also clear that with an increase of ambient temperature, the negative MR will decrease. The observed increase in exponent n with increasing temperature is in agreement with the prediction of the M–S model. The values of n predicted by this theory are less than 0.5. However, the observed values of n in germanium-rich samples are slightly higher than this value. This may be because the M–S model takes into account VRH conduction alone, whereas in the present case two parallel conduction channels are contributing towards the conductivity; these are, VRH conduction, which dominates at low temperatures, and activated-type conduction at higher temperatures.

If conduction takes place in localized states at the band edges, the negative MR is explained by the two-band model [24]. This model assumes the existence of a band of high mobility (extended states) over a band with low mobility (localized states), with a sharp mobility edge between the two bands. On the application of magnetic field, the carriers are dumped into the high-mobility band from the low-mobility band, resulting in negative MR. The source of the positive component at high magnetic fields in this model is the decrease in the mobility of the carriers in the high mobility band on the application of magnetic field. The MR expressed as

$$\Delta\rho/\rho \sim -D\left(\frac{g\mu_B H}{kT}\right)^2 + \alpha H^2 \quad \text{when } g\mu_B H \ll kT \quad (4)$$

and

$$\Delta\rho/\rho \sim B\frac{a+b}{a}\alpha H^2 \frac{kT}{g\mu_B H} - 1 \quad \text{when } g\mu_B H \gg kT \tag{5}$$

where α, D and B are constants, a and b are band parameters, k is Boltzmann's constant, μ_B is Bohr magneton and g the spectroscopic factor. These relations predict a linear field dependence of MR at low temperature and low magnetic fields. However, at finite temperatures this theory gives a square-law dependence. The observed behaviour of negative MR in selenium-rich samples, and in germanium-rich samples at 300 K, is consistent with this model. Furthermore, in both germanium-rich (at 300 K) and selenium-rich samples at high magnetic fields the MR starts decreasing, showing the presence of a positive component. This behaviour is again in agreement with this model.

The decrease in the magnitude of the negative MR with increase in ambient temperature can be attributed to the shift of the charge carriers to higher localized states closer to the mobility edge. The closer are the charge carriers to the mobility edge, the smaller is the change in mobility due to the magnetic field dumping, as a result of which the negative MR will decrease with increasing temperature. It can be seen from Table II that values of n for selenium-rich samples at 300K are closer to two, but deviations are observed at low temperatures in good agreement with the two-band model. Moreover, Table II shows that n increases with increase of selenium content. This behaviour of n is similar to that of the conductivity activation energy, which increases with increasing selenium concentration as found from d.c. conductivity measurements [21] on these samples.

4. Conclusions

Magnetoresistance measurements on amorphous Ge_xSe_{1-x} samples have shown that MR depends upon the type of conduction process involved in a particular sample. The semiclassical random-walk hopping model explains the observed behaviour of MR in germanium-rich samples, where the conduction is characterized by Mott's VRH in the localized states near the Fermi level. However, the MR data for selenium-rich samples are consistent with the prediction of the two-band model.

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References

1. W. SASAKI and De B. OUBOTER, *Physica* **27** (1961) 977.
2. R. P. KHOSLA and J. R. FISCHER, *Phys. Rev.* **B2** (1970) 4084.
3. *Idem, ibid.* **B6** (1972) 4073.
4. M. R. BOON, *ibid.* **B7** (1973) 761.
5. H. ROTH, W. P. STREUB, W. WERNARD and J. E. MUTHEM, *Phys. Rev. Lett.* **11** (1963) 328.
6. G. BAUER and H. KAHLERT, *Phys. Rev.* **B5** (1972) 566.
7. J. F. WOODS and G. Y. CHEN, *ibid.* **135** (1964) A1462.
8. W. SASAKI, *J. Phys. Soc. Jpn.* **20** (1965) 825.
9. C. YAMANOUCHI, K. MIZUGUCHI and W. SASAKI, *ibid.* **22** (1967) 859.
10. Y. KATAYAMA and S. TANAKA, *Phys. Rev.* **153** (1967) 873.
11. H. MELL and J. STUKE, *Phys. Status Solidi* **24** (1967) 183.
12. *Idem, J. Non-Cryst. Solids* **4** (1970) 304.
13. H. MELL, "Proceedings of the 5th International Conference on Amorphous and Liquid Semiconductors", Garmisch, Partenischen, FRG, 1973, edited by J. Stuke and W. Brenig (Taylor and Francis, London, 1974) P. 203.
14. A. M. CLARK, M. H. COHEN, M. CAMPU and H. P. D. LANYON, *J. Non-Cryst. Solids* **16** (1974) 117.
15. H. MELL, thesis, University of Marburg (1973).
16. N. F. MOTT and E. A. DAVIS, "Electron Processes in Non-Crystalline Materials" (Clarendon, Oxford, 1971).
17. B. MOVAGHAR and L. SCHWEITZER, *J. Phys. J. Phys. C* **11** (1978) 125.
18. P. DELHAES, P. De KEPPER and M. UHLRICH, *Phil. Mag.* **29** (1974) 1201.
19. P. DELHAES, *Phys. Chem. Carbon* **7** (1971) 193.
20. R. M. MEHRA, HEMANT KUMAR, SURINDER KOUL and P. C. MATHUR, *Phys. Status Solidi (a)* **83** (1984) 941.
21. R. M. MEHRA, HEMANT KUMAR, SURINDER KOUL and PAWAN SIKKA, *Mater. Chem. Phys.* **11** (1984) 481.
22. J. W. JEFFERY, "Methods in X-ray crystallography" (Academic Press, London, 1971) p. 83.
23. K. YOSIDA, *Phys. Rev.* **107** (1957) 396.
24. E. T. HEDGCOCK and T. W. RAUDORF, *Solid State Commun.* **8** (1970) 1819.
25. Y. TOYOZAWA, *J. Phys. Soc. Jpn.* **17** (1962) 986.
26. R. M. MEHRA, S. C. AGARWAL, SAURABH RANI HEMANT KUMAR and P. C. MATHUR, *J. Non-Cryst. Solids* **69** (1985) 261.

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