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Semiconducting Properties of Nonstoichiometric Manganese Silicides

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Electrical resistivity, Hall coefficient and thermoelectric power were measured on manganese silicides of composition $MnSi_{2-x}$ with x ranging from 0.25 to 0.28 in the temperature range from 80 to 1100K. At higher temperatures a forbidden energy gap estimated from the resistivity data was about 0.40 eV. It was confirmed that $MnSi_{2-x}$ was a degenerated semiconductor and that the hole concentrations in the degenerated state varied from 1.8 to 2.3 $\times$ 10^{21} cm^{-3}. The ratio of electron to hole mobility was less than unity. The intrinsic resistivity and the hole mobility varied with temperature as 3.6 $\times$ 10^{-4} $\exp(2320/T)$ and 1.2 $\times$ 10^{4} $T^{-3/2}$ respectively. The value of Hall coefficient calculated by using a mobility ratio of 0.02 was in good agreement with that observed in the intrinsic region. From the relationship between hole concentration and thermoelectric power for $MnSi_{1.73}$ near room temperature, the hole effective mass was estimated to be twelve times as large as the free electron mass. The calculation of the thermoelectric power was carried out based on the assumptions that the scattering of carriers is dominated by acoustic lattice scattering and that the carriers obey Fermi-Dirac statistics. The calculated results were in reasonable agreement with the observed thermoelectric powers in the temperature range from 150 to 1100 K.

1. Introduction

Many of the 3*d*-transition metal silicides are compounds which have been developed as the materials having a superior heat-resistance [1-3]. Since $CrSi_2$, $MnSi_2$ and β-$FeSi_2$ have semiconducting properties and large thermoelectric power, they can be utilised as thermoelectric conversion elements by which thermal energy is directly changed into the electric power [4-15]. The existence of these disilicides has been reported by Boren [16] and Hansen [17]. However, microphotography, and thermal and X-ray analysis showed that $MnSi_2$ was not an intermetallic compound but was a two-phase alloy of $MnSi_{2-x} + xSi$ [17-25]. For example, $MnSi_{1.72}$ ($x = 0.28$) belongs to a space group D_4^{18} having lattice constants of $a = 5.526$Å and $c = 17.455$Å [20], $Mn_{11}Si_{19}$($x = 0.27$) belongs to D_{2d}^{8} having $a = 5.52$Å and $c = 48.2$Å [21], and Mn_4Si_7 ($x = 0.25$) belongs to D_{2d}^{6} having $a = 5.525$Å and $c = 17.463$Å [25]. On the other hand, the thermoelectric power of $MnSi_{2-x}$ with x ranging from 0.25 to 0.28 has large positive values from 100 to 250 μV/deg at room temperature. However, the details of the thermoelectric power and the conduction mechanism have not yet been clarified.

The purpose of the present study was to examine the conduction mechanism and to calculate the thermoelectric power for $MnSi_{2-x}$ based on the assumptions that the valence band is parabolic and that the holes obey the Fermi-Dirac statistic.

2. Experimental Procedures

Specimens of $MnSi_{2-x}$ with x ranging from 0.20 to 0.30 were prepared by melting mixtures of MnSi and Si single crystal (n-type semiconductor with purity of 99.999%) chips in an argon atmosphere. These specimens were identified by a powder X-ray diffractometer with a curved monochrometer. The specimens with $0.25 \leqq x \leqq 0.28$ were found to be tetragonal D_{2d}^{6} with lattice constants of $a = 5.523 \pm 0.004$Å, $c = 48.21 \pm 0.06$Å and $c/a = 8.73$, and these are in good agreement with those reported by Schwomma [21] and Morokhovets [22]. Furthermore, it was found that specimens with $x > 0.28$ are two-phase alloys composed of $MnSi_{1.72}$ and MnSi, and that specimens with

$x < 0.25$ are two-phase alloys with isolated Si in the $MnSi_{1.75}$. The specimens in the single phase region were cut off into a rectangular parallelepiped form of $1 \times 5 \times 10$ mm^3 and annealed at 1000°C for 5 h in a vacuum of 5×10^{-6} torr.

The measurements of electrical resistivity and Hall coefficient were carried out by a dc method as described by Putley [26]. The Hall coefficient was measured in an applied magnetic field of 6000 gauss. The same method as reported by Sakata [6] was used to measure the thermoelectric power in a hydrogen atmosphere of 100 torr over the temperature range from 80 to 1100 K. The temperature differences between the ends of a specimen laid in the range from 0.3 to 2.0°C. The thermoelectromotive forces were measured on two potentiometers and the values of the thermoelectric power were obtained from the slopes of temperature difference versus thermoelectromotive force. The thermoelectric powers were calibrated and are presented as absolute values.

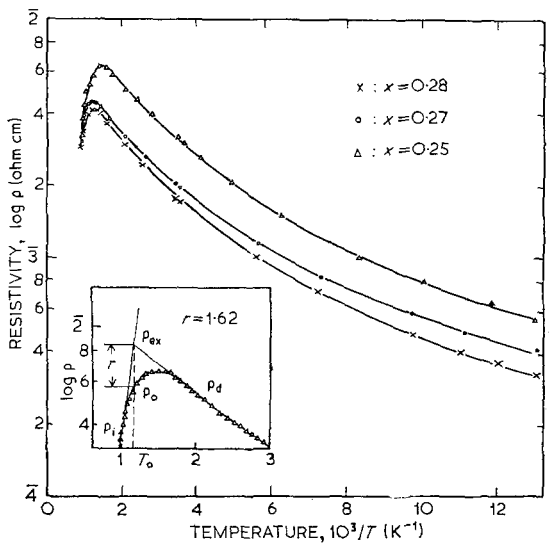

Figure 1 The electrical resistivities as a function of the reciprocal absolute temperature for $MnSi_{2-x}$.

3. Experimental Results

Fig. 1 shows the electrical resistivities as a function of the reciprocal absolute temperature for $MnSi_{2-x}$. At lower temperatures the values of resistivity ρ decrease with increasing x (decreasing Si content), but the general behaviour of all the specimens is the same. These results also indicate that all values of ρ fit on a straight line of $\ln \rho \propto T^{-1}$ at higher temperatures, therefore, the forbidden energy gap E_g is about 0.4 eV and the intrinsic resistivity is expressed by $\rho_i = 3.6 \times 10^{-4} \exp(2320/T)$.

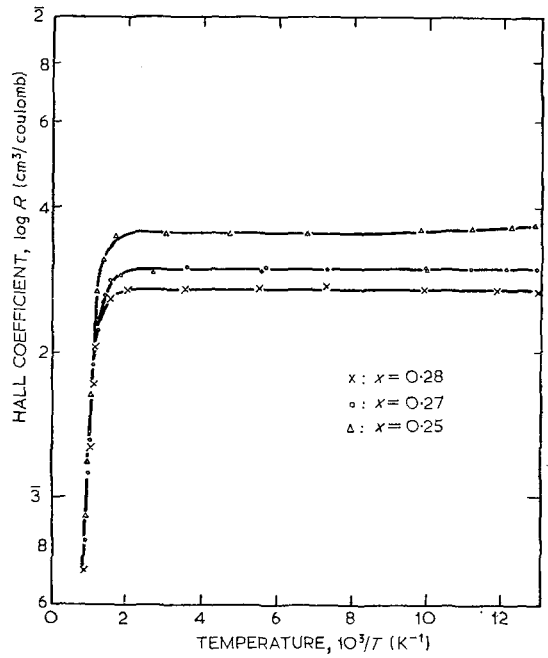

Figure 2 The relationship between Hall coefficient and reciprocal absolute temperature for $MnSi_{2-x}$.

The relationship between Hall coefficient and reciprocal temperature is shown in fig. 2. The sign of the Hall coefficient R is positive for all specimens over the temperature range from 80 to 1100 K. At lower temperatures R is independent of temperature, but its value increases with decreasing x. At higher temperature R decrease remarkably with increasing temperature and indicates a relationship of $\ln (RT^{3/2}) \propto T^{-3}$. The forbidden energy gap E_g obtained from the temperature dependences of R is 0.40 eV, which is in agreement with that of the resistivity data.

Plots of the Hall mobility $\mu_H = R/\rho$ versus reciprocal temperature are shown as relationships of $\ln \mu_H$ to $\ln T^{-1}$ in fig. 3. The values of μ_H decrease with increasing temperature, and all values fit on straight line above room temperature. The hole mobility μ_p obtained from the region above 250 K can be expressed by $\mu_p = 1.2 \times 10^4 T^{-3/2}$. Fig. 5 shows the temperature dependence of the thermoelectric power. The curves of thermoelectric power α increase with increasing

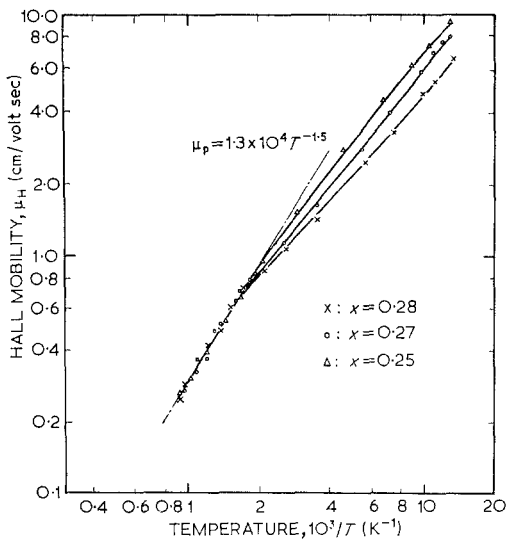

Figure 3 Plots of the Hall mobility versus reciprocal absolute temperature for $MnSi_{2-x}$.

temperature at lower temperatures and shows a maximum value at about 800 K, they also increase with decreasing x over the temperature range investigated. The signs of α for all specimens are positive over the entire temperature range. These observed signs are in agreement with those of R.

4. Discussions

4.1. Electron and Hole Concentrations

From figs. 1 and 2 which show the temperature dependences of ρ and R, it appears that $MnSi_{2-x}$ is a degenerated semiconductor and that the ratio of electron mobility μ_e to hole mobility μ_p is less than unity. For the specimens with $x = 0.25$, 0.27 and 0.28, the hole concentrations are 1.8, 2.2 and 2.3 $\times$ 10^{21} cm^{-3}, respectively, and these values are independent of temperature below 600 K. It is also possible to estimate the value of mobility ratio $b = \mu_e/\mu_p$ from the relationship between electron concentration n and hole concentration p for both intrinsic and extrinsic resistivities. The values of b were estimated by the method described by Hunter [27]. As seen in fig. 1, the curve of extrinsic resistivity ρ_d can be extrapolated to meet a straight line of intrinsic resistivity ρ_i. From this interaction point, a resistivity value ρ_{ex} and a temperature T_0 are determined. At the temperature T_0, a resistivity value ρ_0 is determined from the ρ data. If the ratio ρ_{ex}/ρ_0 is replaced by r, the mobility ratio for a p-type semiconductor is given by

$$b = \frac{1}{r - 1} - r . \tag{1}$$

From the precise data of ρ and equation 1, the values of b are found to be 0.01 to 0.03 for the specimens investigated. Using the relationship between ρ, b and μ_p, the carrier concentrations and R in the intrinsic region can be estimated from following the equations [28]

$$n_s = p - n , \tag{2}$$

$$p = \left(\frac{1}{e\rho\mu_p} + bn_s\right)\Big/(n + 1) \cdot \tag{3}$$

$$R = \frac{p - nb^2}{e(nb + p)^2} , \tag{4}$$

where n_s and e are the hole concentration in the degenerated state and the free electron charge, respectively. These values were calculated by using $b = 0.02$ and the ρ and R data in the intrinsic region, and the results are tabulated in table I. Both electron and hole concentrations calculated by using the two functions $\rho_i = 3.6 \times 10^{-4} \exp(2320/T)$ and $\mu_p = 1.2 \times T^{-3/2}$ for $MnSi_{1.73}$ are illustrated as solid line in fig. 4. As seen in table I and fig. 4, the observed Hall coefficients R_{obs} are in good agreement with the calculated values R_{cal}, and also the observed hole concentrations agree well with the calculated values. Therefore, it appears firstly that the value of b for $MnSi_{2-x}$ is smaller than unity and is in fact close to the value of 0.02 used in the calculations, and secondly that holes dominate the intrinsic conduction in $MnSi_{2-x}$.

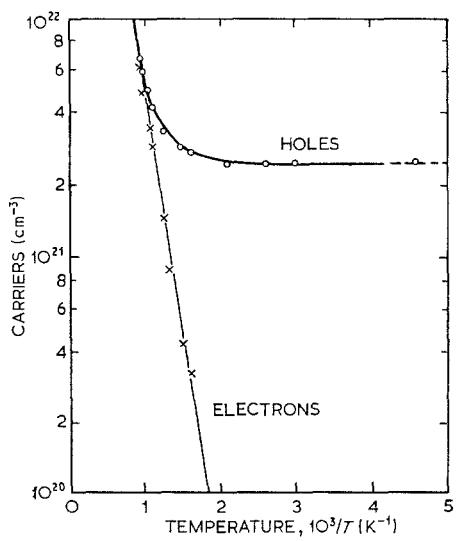

Figure 4 Concentration of electrons and holes in $MnSi_{1.73}$, the solid line and curve are the calculated values.

TABLE I The electron and hole concentration n, p and Hall coefficient R for $MnSi_{2-x}$ in the intrinsic region, R_{cal} and R_{obs} are calculated and observed Hall coefficient, respectively.

Kind/Samples	T (K)	p (cm^{-3})	n (cm^{-3})	R (cm^3/coulomb)	
				R_{cal}	R_{obs}
$x = 0.28$	1099	7.49×10^{21}	5.17×10^{21}	0.81×10^{-3}	0.8×10^{-3}
	980	4.98	2.66	1.21	1.3
$r_t = 2.32 \times 10^{21}$	893	4.08	1.76	1.51	1.5
	813	3.35	1.03	1.84	1.9
$x = 0.27$	1088	7.39×10^{21}	5.23×10^{21}	0.83×10^{-3}	0.8×10^{-3}
	1000	5.44	3.28	1.17	1.1
$n_s = 2.16 \times 10^{21}$	970	4.66	2.50	1.36	1.3
	910	4.02	1.86	1.58	1.6
$x = 0.25$	1080	7.16×10^{21}	5.38×10^{21}	0.86×10^{-3}	0.9×10^{-3}
	1010	5.25	3.47	1.17	1.2
$n_s = 1.78 \times 10^{21}$	950	3.84	2.01	1.66	1.6
	830	2.82	1.04	2.38	2.5

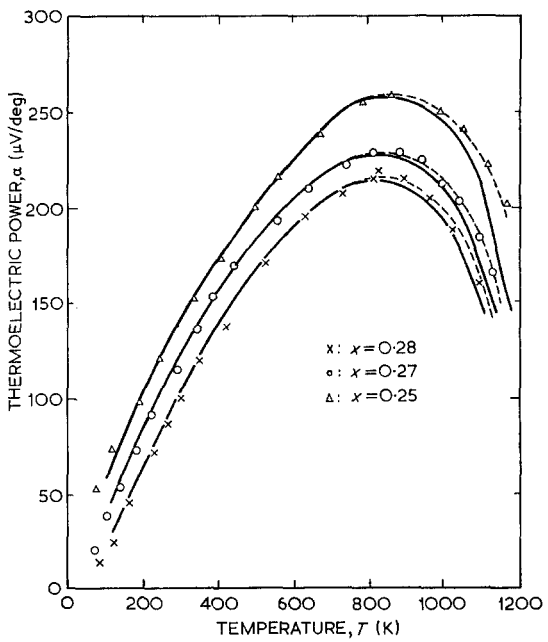

Figure 5 The temperature dependences of thermoelectric power for $MnSi_{2-x}$, the solid and the dotted curves represent the calculated values.

4.2 Analysis of Thermoelectric Power

As seen in fig. 5, the thermoelectric power α has large positive values in spite of the fact that electrons and the holes coexist in a specimen above 800 K. This result suggests that holes determine the α values in the high temperature region. An equation as described by Ioffe [29] was used in the analysis of the temperature dependence of α over the temperature range investigated. The equation is given by

$$\alpha = \pm \frac{k}{e} \left\{ \frac{\int_0^\infty \frac{df_0(\epsilon^*)}{d\epsilon^*} l(\epsilon^*)\, \epsilon^{*2}\, d\epsilon^*}{\int_0^\infty \frac{df_0(\epsilon^*)}{d\epsilon^*} l(\epsilon^*)\, \epsilon^*\, d\epsilon^*} - \mu^* \right\} \quad \ldots\ldots (5)$$

where $f_0(\epsilon^*)$ is a thermal equilibrium energy distribution function of the carriers, $l(\epsilon^*)$ is the mean free path of carriers and is a function of energy, ϵ^* is the kinetic energy of carriers in units of kT, and $\mu^* = \mu/kT$ is the reduced chemical potential. The + and − signs correspond to holes and electrons, respectively. On the basis of the assumptions that acoustic lattice scattering is the dominant scattering mechanism and that $f_0(\epsilon^*)$ follows Fermi-Dirac statistic because $MnSi_{2-x}$ is a degenerated semiconductor, equation 5 can be expressed as

$$\alpha = \pm \frac{k}{e} \left\{ 2 \frac{F_1(\eta^*)}{F_0(\eta^*)} - \eta^* \right\}, \qquad (6)$$

where η^* is either the reduced Fermi energy of holes or of electrons, and $F_r(\eta^*)$ is a well-known function called a Fermi-Dirac integral and is given by

$$F_r(\eta^*) = \frac{\epsilon^{*r}\, d\epsilon^*}{\exp(\epsilon^* - \eta^*) + 1} \qquad (7)$$

On the other hand, when both holes and electrons are present α is given by

$$\alpha = \rho\{(\alpha_p/\rho_p) + (\alpha_e/\rho_e)\}, \quad (8)$$

where α_p and α_e are the partial thermoelectric powers of holes and of electrons respectively, and ρ_p and ρ_e are the resistivities corresponding to holes and electrons, respectively. Using the relation $kT(\eta_p^* + \eta_e^*) = -Eg$, where η_p^* and η_e^* are the reduced Fermi energies of holes and of electrons, respectively, equation 8 can be written as

$$\alpha = \frac{k}{e(nb+p)}\left[2p\frac{F_1(\eta_p^*)}{F_0(\eta_p^*)} - nb\left\{2\frac{F_1(-\eta_p^* - Eg/kT)}{F_0(-\eta_p^* - Eg/kT)} + \frac{Eg}{kT}\right\} - \eta_p^*(nb+p)\right] \quad (9)$$

If the valence band is parabolic, the hole concentration is given by

$$p = \frac{4\pi(2m_p^* kT)^{3/2}}{h^3} F_{1/2}(\eta_p^*), \quad (10)$$

where m_p^* and h are the effective mass of holes and Planck's constant. To calculate the temperature dependence of α for $MnSi_{2-x}$, an m_p^* is estimated from p and α of the specimen having $x = 0.27$ by using equations 6 and 10 near room temperature. This gives an m_p^* that is twelve times as large as a free electron mass m_0. Using a constant value of $m_p^* = 12\,m_0$ and the hole concentrations at various temperatures the values of η_p^* were estimated from equation 10, and these were then used in equation 9 to calculate the temperature dependence of α. The experimentally determined values of $b = 0.02$ and of $E_g = 0.40$ eV were also used in the calculation. The results are shown as the solid lines in fig. 5. The calculated values of α are in relatively good agreement with those observed over the temperature range from 150 to 1100 K, thus confirming that the hole effective mass has large value which is of the order of $m_p^* = 12\,m_0$. In the temperature region where both holes and electrons are present, however, the values of α calculated from equation 9 are shown to be smaller than those obtained from equation 6 (dotted line), about 10% smaller at 1100 K. The calculated values which neglected the contribution of electrons (i.e. those from equation 6) are in reasonable agreement with the observed values. This, in fact, indicates that the ratio of electron to hole mobility is considerably less than the value of 0.02 obtained from the resistivity data, although the latter value gives good agreement between the observed and calculated values of the Hall coefficient R. The reason for this anomaly is not clear at the present time.

5. Conclusion

The nonstoichiometric compound $MnSi_{2-x}$ with x ranging from 0.25 to 0.28 is a degenerated semiconductor and the hole concentration in the degenerated state increases with increasing x. The forbidden energy gap is estimated to be about 0.40 eV and intrinsic resistivity can be represented by $\rho_i = 3.6 \times 10^{-4} \exp(2320/T)$. The ratio of electron to hole mobility is $b \leqq 0.02$ and the Hall coefficient calculated by using $b = 0.02$ shows good agreement with that observed above 600 K. Above room temperature the hole mobility is expressed by $\mu_p = 1.2 \times 10^4\, T^{-3/2}$ and is in reasonable agreement with the Hall mobility. An effective mass for holes estimated from the relationship between the thermoelectric power and the hole concentration near room temperature is found to be twelve times as large as a free electron mass.

The temperature dependences of thermoelectric power calculated by using this effective mass is in good agreement with that observed in the temperature range from 150 to 1100 K.

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