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Half-metallic ferromagnets: II. Transport properties of NiMnSb and related inter-metallic compounds

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Abstract. The electrical resistivity and the Hall effect of inter-metallic compounds XMnSb (X = Pt, Ni, Au) and PtMnSn were investigated in the temperature region 4–1000 K. The results for the anomalous Hall effect were analysed in terms of skew scattering and side-jump contributions. This analysis is possible in a half-metallic ferromagnet because the conduction electron spin polarisation at $T = 0$ K is known.

1. Introduction

The inter-metallic compounds NiMnSb and PtMnSb are examples of an interesting class of magnetic materials, the so-called half-metallic ferromagnets (de Groot *et al* 1983). These compounds are ferromagnets with a high Curie temperature. The magnetic moments in these materials are localised for the main part on the Mn atoms; in addition there are holes in a broad valence band of mainly Sb 5p orbitals, which also contribute to the magnetic moments. Band-structure calculations (de Groot *et al* 1983) show that the band for minority spin electrons has a gap at the Fermi level, whereas the Fermi level intersects the band for majority spin electrons. The complete spin polarisation of the charge carriers makes it interesting to investigate the transport properties, in particular the (anomalous) Hall effect.

In this paper we report measurements of the electrical resistivity and the Hall effect of several compounds XMnSb (X = Pt, Ni, Au) and PtMnSn, some of which are half-metallic ferromagnets. In a previous publication we already reported on the preparation, the microstructure and the magnetic properties of these materials (Otto 1987, Otto *et al* 1989). It was shown that the quality of the samples depends on the method of preparation and heat treatment. For our transport measurements reported here, we used only samples with the best stoichiometry, single phase (if possible) and with the lowest atomic disorder. Samples of NiMnSb, PtMnSb, PtMnSn, CuMnSb and CoMnSb were single-phase stoichiometric materials. The sample AuMnSb contained $4 \pm 1\%$ MnSb, corresponding to a composition $Au_{1.08}MnSb$ of the main phase. Atomic disorder was small in the PtMnSb samples. In the NiMnSb sample used (annealed sample) the atomic disorder is small at low temperature, but it increases at temperatures higher than 800 °C.

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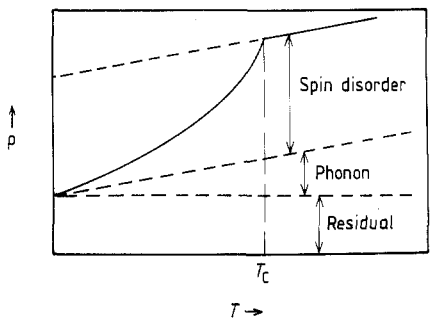

Figure 1. Schematic respresentation of the contributions to the resistivity of magnetic metals.

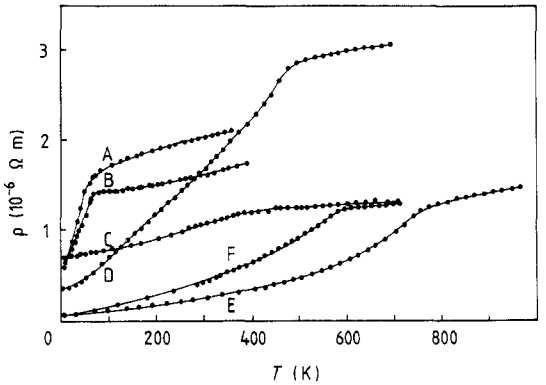

Figure 2. Electrical resistivity ρ as a function of temperature: A, CuMnSb; B, AuMnSb; C, PtMnSn; D, CoMnSb; E, NiMnSb; F, PtMnSb.

Appreciable atomic disorder is an intrinsic property of the compounds PtMnSn, CuMnSb and CoMnSb and cannot be avoided.

2. Electrical resistivity

The electrical resistivity of rectangular polycrystalline samples was measured with the four-point method in the temperature region 4–800 K. We used silver paste for the contacts. The absolute accuracy of the transport measurements (resistivity and Hall effect) is generally of the order of 1%. The scattering of the points of the figures gives a good indication of the relative precision.

The electrical resistivity of magnetic metals has the characteristic temperature dependence shown schematically in figure 1. The resistivity ρ is due to scattering of charge carriers at lattice defects (impurity atoms or atomic disorder), lattice vibrations (phonons) and spin disorder. The contribution of phonons increases with increasing temperature and is proportional to T at high temperature. The scattering at lattice defects is independent of temperature (at least for a temperature-independent band structure and atomic disorder), and equal to ρ at $T = 0$ (residual resistivity). In magnetic metals there is a large contribution to the resistivity due to spin disorder. This contribution increases with increasing temperature up to the Curie temperature T_C and remains approximately constant above T_C (de Gennes and Friedel 1958).

The observed resistivity ρ as a function of the temperature of the investigated compounds is shown in figure 2. All materials show the behaviour characteristic for

Table 1. Electrical resistivity of NiMnSb and related compounds: ρ_0, residual resistivity ($T = 0$); $\rho_{sd}(T_C)$, spin-disorder contribution at T_C; and ρ_{phonon}/T, slope of phonon contribution determined from data above T_C.

Compound	$\rho_0(T=0)$ ($10^{-8}\ \Omega$ m)	$\rho_{sd}(T_C)$ ($10^{-8}\ \Omega$ m)	ρ_{phonon}/T ($10^{-10}\ \Omega$ m K^{-1})
NiMnSb	7	70 ± 30	14
PtMnSb	7	86	5
PtMnSn	69	36	4
AuMnSb	59	81	4–16
CuMnSb	59	100	13
CoMnSb	37	205	9

magnetic metals. The curves exhibit a pronounded change of slope near the magnetic ordering temperature. Indeed we find a very sharp peak in the curve of $d\rho/dT$ against T. Such a sharp peak is expected at the Curie temperature (Fisher and Langer 1968). The Curie temperatures T_C determined in this way correspond closely to the values obtained from magnetic measurements.

We have made a crude analysis of the resistivity in terms of the contributions discussed above; the results are given in table 1. We assumed that the spin-disorder contribution is constant above T_C. Moreover, we also assumed that the phonon contribution is proportional to T in the complete temperature range. For a more accurate analysis it is necessary to use, for example, the Bloch–Grüneisen theory (Ziman 1969), but the values of the Debye temperature for the Heusler alloys are not known. The errors involved in the approximation used are small for the values reported in table 1.

The data show a very large residual resistivity for PtMnSn, AuMnSb, CuMnSb and CoMnSb, indicating a significant atomic disorder. The residual resistivity of NiMnSb is strongly influenced by annealing; it decreases from $17 \times 10^{-8}\ \Omega$ m to $7 \times 10^{-8}\ \Omega$ m after annealing for 15 d at 700 °C and slow cooling. This indicates a decrease of atomic disorder as a result of annealing. The resistivity of CoMnSb measured with increasing temperature showed a large peak at about 400 K. After heating the sample to 750 K and cooling, the peak disappeared and it remained absent after repeated heating of the sample. We conclude that the ordering of the atoms in CoMnSb improved during annealing in the temperature region 400–550 K. The curve shown in figure 2 represents data for a well annealed sample.

The linear increase of the resistivity above T_C is anomalously large in NiMnSb and CuMnSb as compared with the other compounds. Since we would not expect large differences in the phonon contribution, the strong increase of ρ above T_C in NiMnSb and CuMnSb probably has a different origin, for example the variation of the density of states at the Fermi level due to spin depolarisation of the valence band. This causes an uncertainty in the estimated value of the phonon contribution at low temperature, so the spin-disorder contribution can be estimated only roughly. Resistivity data for PtMnSn obtained after annealing at 200, 400, 600 and 800 °C were not reproducible. However, the resistivities of arc-melted and quenched PtMnSn were reproducible; these data are shown in figure 2 and table 1.

CuMnSb is an antiferromagnet but the ρ against T curve is very similar to that of the ferromagnetic alloys.

The resistivity of ferromagnetic metals at low temperature usually has a term proportional to T^2, ascribed to one-magnon scattering of conduction electrons (spin-flip

scattering) (Mannari 1959). In our resistivity data for CoMnSb, NiMnSb and PtMnSb there is little or no evidence for such a T^2 contribution. Indeed, in a half-metallic ferromagnet at low temperature all states at the Fermi level are spin polarised, and spin-flip scattering is not possible. Thus for a half-metallic ferromagnet one expects the absence of a T^2 term in the resistivity.

3. Experimental results of the Hall effect

The ordinary Hall effect in metals and semiconductors is caused by the Lorentz force on the charge carriers and is proportional to the applied magnetic field. In ferromagnetic materials there is an additional contribution, the so-called anomalous Hall effect (AHE), which is proportional to the magnetisation (Hurd 1972). The total resistivity is given by

$$\rho_{yx} = E_y/j_x = R_o B_z + R_s \mu_0 M_z \tag{1}$$

where E_y is the Hall field, j_x the current density. The z component of the magnetic induction in the sample is $B_z = \mu_0[H_A + (1 - N_D)M_z]$, H_A is the applied magnetic field parallel to the z axis, N_D is the demagnetising factor and μ_0 is the magnetic permeability of vacuum.

We have measured the Hall resistivity as a function of applied magnetic field in the temperature region 4–800 K. The measurements were carried out using sensitive AC Hall equipment constructed in our laboratory. This equipment employs an 82 Hz AC source, which prevents the interference of thermal gradients and thermomagnetic effects. Low-temperature measurements were carried out in an Oxford cryostat with a superconducting magnet that could be switched within 1 s between +3 and −3 T. A detailed description of the equipment for high-temperature (295–1000 K) and low-temperature (4–300 K) Hall measurements is given by Otto (1987) and van der Heide (1982), respectively.

The rectangular samples used for Hall measurements were shaped from polycrystalline ingots, with five contacts made with silver paste; two contacts were used to compensate for spurious voltages at $H_A = 0$ caused by misalignment of contacts.

As an example we show in figure 3 measurements of Hall resistivity isotherms for PtMnSb. The curves for temperatures below T_C show an almost linear increase of ρ_{yx}, followed by a knee and a second linear part of smaller slope. The field at which the knee occurs corresponds to the maximum demagnetising field in the Hall sample. Thus the measurements clearly show the anomalous contribution to the Hall effect, corresponding to the second term in (1). The coercive fields measured by us were quite small (about 0.005 T). The analysis of the Hall effect data in terms of R_o and R_s depends in a sensitive way on the precise value of the magnetisation as a function of T and H_A. Therefore we always used magnetisation data obtained on samples that were prepared and annealed in precisely the same way as the samples used for transport measurements. The magnetisation data were reported earlier (Otto 1987, Otto *et al* 1989). In most of the literature the coefficients R_o and R_s are calculated without taking into account the internal magnetic susceptibility χ_i above the technical saturation. Since we also measured the Hall effect at temperatures close to T_C, where χ_i is large, the correction for χ_i had to be taken into account. The data for AuMnSb were corrected for the presence of a small amount of ferromagnetic MnSb in the sample (Otto 1987).

From a thorough analysis of the data we deduced values of the ordinary Hall coefficient R_o. We were not able to obtain reliable values of R_o at high temperatures, above

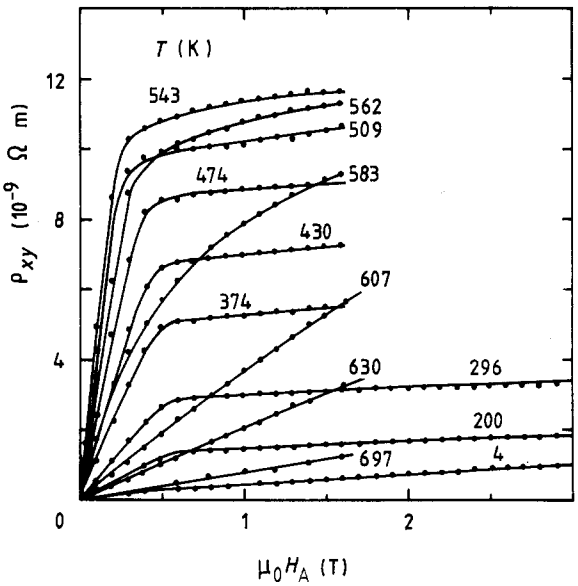

Figure 3. Hall resistivity ρ_{yx} of PtMnSb as a function of applied magnetic field H_A.

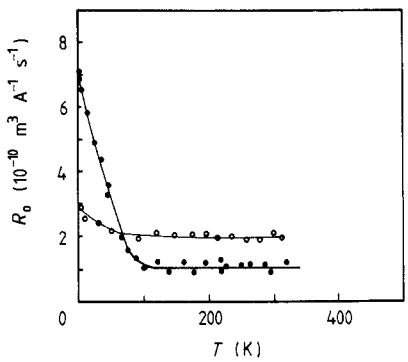

Figure 4. Ordinary Hall coefficient R_0 as a function of temperature for PtMnSb (○) and NiMnSb (●).

T_C. The temperature dependence of R_0 for PtMnSb and NiMnSb is shown in figure 4. The value of R_0 is temperature-independent at high temperature and increases at low temperatures. The values of R_0 for AuMnSb, PtMnSn and CoMnSb could not be determined accurately. The data for AuMnSb indicate a small decrease between 4 and 33 K; at higher temperature R_0 increases again and reaches a constant value at $T > 235$ K. The value of R_0 for PtMnSn is independent of temperature up to 210 K and increases between 210 K and $T_C = 330$ K. The results for the ordinary Hall effect of CoMnSb were very inaccurate; the spread of points was so large that only its negative sign is certain. This indicates that in CoMnSb electrons are the main current carriers. In all other Heusler alloys studied, R_0 is positive, indicating holes as the main current carriers. A survey of the hole concentration p, expressed in holes per formula unit, deduced from R_0 with the equation $p = 1/R_0 e$ is given in table 2.

Results for the coefficient R_s of the anomalous Hall effect as a function of temperature are given in figure 5. The curves all show a strong increase of R_s with increasing

Table 2. Hole concentration p (holes per formula unit) calculated from the ordinary Hall coefficient R_0 with $p = 1/R_0 e$.

Compound	Type	At 4.2 K	At high temperature
PtMnSb	p	1.3	1.9 ($T > 50$ K)
NiMnSb	p	0.45	2.8 ($T > 94$ K)
CoMnSb	n	—	—
AuMnSb	p	0.31	0.47 (33 K) 0.31 ($T > 235$ K)
PtMnSn	p	1.9	1.9 ($T < 210$ K)

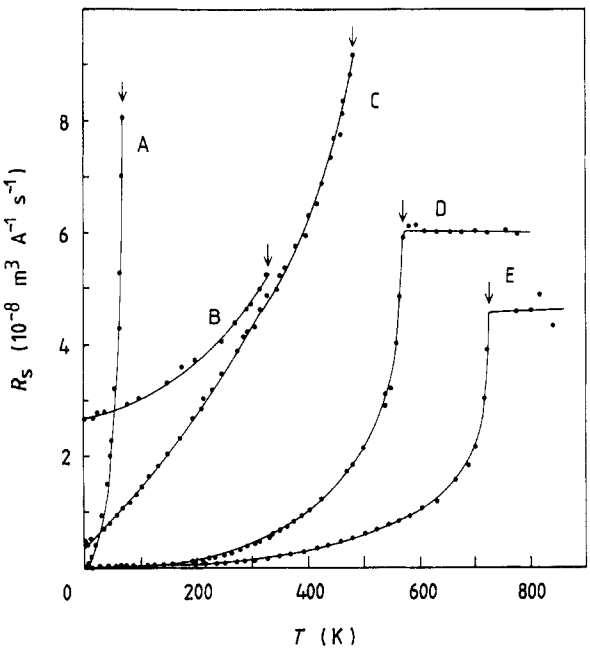

Figure 5. Anomalous Hall coefficient R_s of PtMnSb, NiMnSb, CoMnSb, AuMnSb and PtMnSn as a function of temperature. The Curie temperatures are indicated by arrows. A, AuMnSb; B, PtMnSn; C, CoMnSb; D, PtMnSb; E, NiMnSb.

temperature up to T_C. Above T_C, R_s remains approximately constant, but the values obtained in this region are not very accurate. For all compounds except PtMnSn, R_s is approximately zero at 4 K. However, for PtMnSn, R_s is large at 4 K and its value increases only by a factor two between 4 K and T_C. This effect is directly related to the large residual resistivity in PtMnSn; apparently the low-temperature scattering at crystal defects in PtMnSn is also very effective for the asymmetric scattering which causes the anomalous Hall effect.

4. Discussion of Hall effect results

We discuss first the results obtained for the ordinary Hall effect. The observation of a positive ordinary Hall effect is in agreement with band-structure calculations for

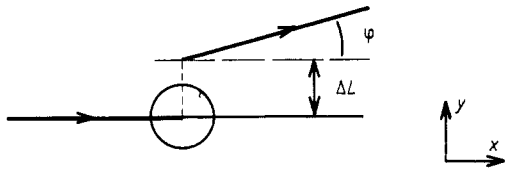

Figure 6. Asymmetric scattering of a charge carrier with spin up (↑), due to skew scattering φ and side jumps ΔL. For an electron with spin down (↓) $\varphi \rightarrow -\varphi$ and $\Delta L \rightarrow -\Delta L$. The magnetisation is parallel to z; the spin-up and spin-down polarisations refer to the z axis.

NiMnSb, PtMnSb and PtMnSn (de Groot *et al* 1983), which show that electrical conduction is due to holes in a partly occupied Sb 5p band. However, the hole concentrations expected from the band-structure calculations ($p = 1$ for NiMnSb, PtMnSb; $p = 2$ for PtMnSn) do not agree with the values deduced from the Hall data with the relation $p = 1/R_0 e$. Moreover, in several materials the apparent hole concentration $p = 1/R_0 e$ depends on the temperature. However, the Hall coefficient in cubic metals generally differs from $1/pe$. This occurs if the Fermi surface is not spherical and also if it consists of more than one sheet (Hurd 1972, Tsuji 1985). This is certainly the case for NiMnSb (Hanssen and Mijnarends 1986), and probalby also for the other Heusler alloys. The Fermi surface of NiMnSb consists of three hole sheets, which are quite anisotropic. Parts of the Fermi surface are even electron-like, resulting in a negative contribution to R_0. For a complicated Fermi surface (e.g. with open orbits) the scattering can be anisotropic in k-space and temperature-dependent. Then the contributions to the Hall effect from different parts of the Fermi surface are also temperature-dependent. The total Hall effect is given by

$$R = \sum_i (\sigma_i^2/\sigma^2) R_{0i} \tag{2}$$

where R_{0i} is the Hall coefficient of the ith part of the Fermi surface, σ_i is its conductivity and σ is the total conductivity (Dugdale and Firth 1969). In such a case the ordinary Hall coefficient depends on temperature in a complicated way and does not allow a simple quantitative interpretation.

In order to give a further interpretation of the anomalous Hall effect (AHE) data, we discuss briefly the theory (Smit 1958, Berger 1970, Berger and Bergmann 1980, Kondo 1962, Nozières and Lewiner 1973, Asomoza *et al* 1983). The AHE is caused by asymmetric scattering of the charge carriers, with two contributions—the skew scattering and the side-jump contribution (figure 6). The sign of the asymmetric scattering changes with the spin polarisation of the charge carriers. The skew scattering depends on details of the scattering potential; only in simple cases of spin-disorder scattering is this contribution proportional to the resistivity. The side-jump contribution originates from the electrical polarisation of the charge carriers due to spin–orbit coupling and is independent of the details of the scattering potential.

We use a simple semi-classical description for further analysis of the anomalous Hall effect. Consider a metal with $p_\uparrow$ charge carriers with spin up, $p_\downarrow$ with spin down; $p = p_\uparrow + p_\downarrow$; $\Delta p = p_\uparrow - p_\downarrow$. An electrical field E_x induces an electrical current $j_x = pe\langle v_x \rangle$, where $\langle v \rangle$ is the average (drift) velocity of the charge carriers. Because of skew scattering and side jumps, the y coordinate of the charge carriers changes in a time interval $\mathrm{d}t$ by

$$\mathrm{d}y = (\tan \varphi + \Delta L/\lambda) v_x \, \mathrm{d}t. \tag{3}$$

This results in a current

$$j_y = \Delta p e \langle v_x \rangle (\tan \varphi + \Delta L/\lambda). \tag{4}$$

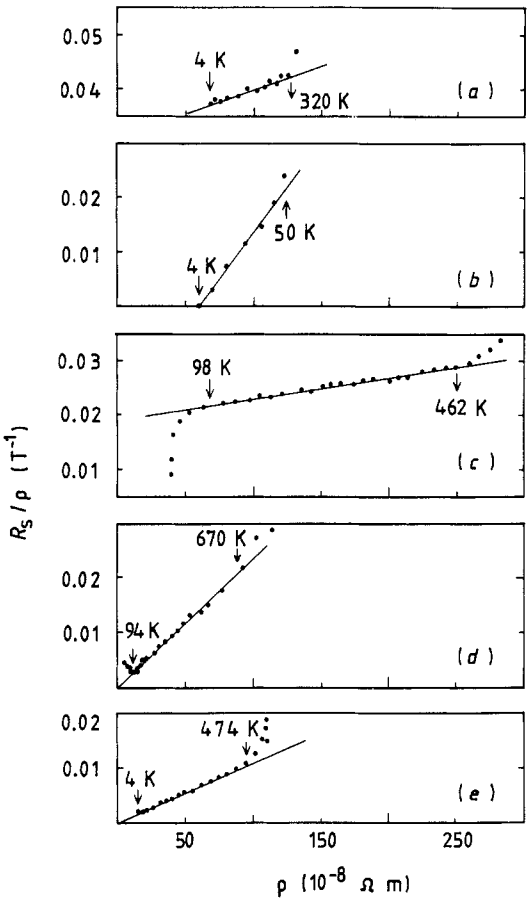

Figure 7. Dependence of R_s/ρ on ρ for several Heusler alloys. The straight lines are linear fits to the experimental points. (*a*) PtMnSn, (*b*) AuMnSb, (*c*) CoMnSb, (*d*) NiMnSb, (*e*) PtMnSb.

In these equations λ is the mean free path of the charge carriers between two scattering events which produce the side jump ΔL. With $\rho_{yx} = \rho(j_y/j_x)$ we obtain

$$\rho_{yx} = (\Delta p/p)\rho(\tan\varphi + \Delta L/\lambda). \tag{5}$$

The mean free path λ is directly related to the ordinary resistivity ρ by $\lambda = m^* v_F/pe^2\rho$, where v_F is the Fermi velocity.

We now make the crucial assumption that the spin polarisation of the charge carriers $\Delta p/p$ is proportional to the net magnetisation:

$$\Delta p/p = \alpha\mu_0 M_z. \tag{6}$$

Using this assumption, we obtain

$$R_s = \alpha[\rho\tan\varphi + (pe^2/m^* v_F)\rho^2\Delta L]. \tag{7}$$

We find that R_s can be written as $R_s = a\rho + b\rho^2$; the term proportional to ρ is due to skew scattering; the term proportional to ρ^2 is due to the side-jump contribution. This ρ-dependence can be used to separate the two contributions.

In figure 7 we have plotted R_s/ρ against ρ for several Heusler alloys and we indeed

Table 3. Skew scattering and side-jump contributions to the anomalous Hall effect.

Compound	Temperature range	a (T^{-1})	b ($T^{-1}\,A^2\,s^2\,kg^{-1}\,m^{-1}$)	φ (deg)	ΔL (Å)
NiMnSb	$0.13 < T/T_C < 0.91$	-6.5×10^{-4}	21500	−0.037	0.48
PtMnSb	$T/T_C < 0.80$	-3×10^{-4}	23000	−0.017	0.43
AuMnSb	$T/T_C < 0.65$	-2.2×10^{-4}	36500	−0.76	0.56
CoMnSb	$0.2 < T/T_C < 0.97$	$+\frac{1}{3} \times 10^{-2}$	3700	+1.1	0.08
PtMnSn	$T/T_C < 0.97$	$+3.15 \times 10^{-2}$	8500	+1.2	0.14

find the expected linear behaviour. From these plots we can obtain values of a and b, and also φ and ΔL, assuming that $\alpha = 1/\mu_0 M_z\,(T = 0)$ (this is the case only for complete spin polarisation at $T = 0$, as is the case for a half-metallic ferromagnet), and using $m^* v_F = \hbar k_F = (6\pi^2 p)^{1/3}$ (for one charge carrier per formula unit, in case of complete spin polarisation). The values of φ and ΔL obtained in this way are given in table 3.

This approach to resistivity and temperature dependence of the spontaneous Hall effect gives a simple explanation of the simultaneous presence at $T = 0$ K of a very small spontaneous Hall coefficient R_s and a large residual resistivity ρ_0 in AuMnSb. (In PtMnSn at $T = 0$ K both ρ_0 and R_s are large.) The reason is that in AuMnSb the contributions of skew scattering and side jump have opposite sign and nearly compensate each other.

The fact that R_s/ρ against ρ gives a straight line shows that the coefficients a and b are independent of temperature. This is possible only if φ and ΔL are independent of temperature, and if the charge-carrier spin polarisation $\Delta p/p$ is indeed proportional to the magnetisation.

The values of the side jump ΔL are nearly the same for NiMnSb, PtMnSb and AuMnSb. The smaller value for PtMnSn is probably due to the incomplete spin polarisation, so for α it is not correct to use the value $1/\mu_0 M_z\,(T = 0)$. The large φ-values for CoMnSb and PtMnSn are interesting; it is not clear why these values are much larger than the values obtained for the other alloys. For CoMnSb this might be due to the contribution from the orbital scattering at the magnetic Co atoms.

5. Conclusions

We have presented measurements of the electrical resistivity and the Hall effect of NiMnSb and related inter-metallic compounds and discussed the results in terms of a simple phenomenological theory. The anomalous Hall effect was separated into two contributions; it was found that the side-jump contribution dominates over the contribution of skew scattering. We remark that the equations used probably only give a good description if the asymmetric scattering of the charge carriers is mainly due to spin-disorder scattering and not to orbital scattering. This is indeed the situation in PtMnSb, NiMnSb, AuMnSb and PtMnSn. The Mn 3d shell in these compounds is completely occupied for one spin direction and empty for the other; so magnetic Mn atoms, responsible for the scattering, carry no orbital moment. Therefore skew scattering will involve mainly the strong spin–orbit interaction of the charge carriers (holes in the Sb 5p band).

It was possible to separate the contributions of skew scattering and side jump to the anomalous Hall effect by assuming a proportionality between the spin polarisation of the charge carriers and the total magnetisation (which is due mainly to the local moments

on Mn). Such a proportionality is not at all obvious and is in fact an important indication of the way in which the electronic structure of these materials changes with increasing temperature. This question has been addressed in a previous publication (Otto *et al* 1987).

We have reported quantitative values of φ and ΔL. This was possible because in a half-metallic ferromagnet the charge-carrier spin polarisation is known. Unfortunately, a theory for quantitative calculation of the asymmetric scattering parameters φ and ΔL is not available, so a comparison with experimental values is not yet possible. We hope that such a theory will be developed in the near future.

Acknowledgments

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