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Electrical resistivity and absolute thermoelectric power of liquid indium–nickel–manganese ternary alloys

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Abstract. The electrical resistivity and the absolute thermopower of In–Ni–Mn liquid ternary alloys have been measured as functions of temperature and of concentration. The transition metal composition was held constant and, starting from the indium–nickel eutectic, we substituted manganese for nickel up to 50 atomic per cent manganese ($\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$ with x up to 0.5). The experimental transport properties for the ternary alloys are completely different from what could be expected from an interpolation between the resistivities of the two binary systems In–Ni and In–Mn that we measured earlier. Therefore this system is particularly suitable for testing the extended Faber–Ziman theory. Experimentally it is found that the resistivity decreases and that the thermopower increases strongly as functions of the manganese composition in the ternary system. These data are discussed and interpreted qualitatively, taking into account the electronic structure of the ternary alloy.

1. Introduction

The purpose of this paper is to present and to discuss a new set of experimental values of the electrical resistivity ρ and of the absolute thermopower Q of the liquid ternary alloys $\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$, each containing a polyvalent metal and two transition metals. For simple polyvalent metals such as indium, the current is considered to be carried in an s–p conduction band and the electronic transport properties are well described by the nearly free-electron theory. However, when polyvalent metals are alloyed with 3d elements, the situation is less clear because of the presence of d electrons in the conduction band, which may cause an important modification in the simple-metal transport properties. Generally in a polyvalent–3d binary alloy the resistivity increases with the concentration of the 3d metal [1]. Until now the absolute thermoelectric power (ATP) of manganese had not been measured due to its reactivity with the container and the electrodes (liquid manganese at 1250 °C dissolves all metals apart from tungsten) and to the high melting point of the transition metal. However, from the extrapolations of the thermopowers of the binary systems In–Mn [2] and In–Ni [3, 4] it can be expected to be positive.

First we describe briefly the experimental method and the results in section 2. We recall in section 3 the basic formulae for the resistivity and the thermoelectric power, and explain qualitatively our experimental results in terms of the extended Faber–Ziman theory. We discuss the resistivity and the ATP versus energy using the electronic structures $3d^54s^2$ for manganese and $3d^84s^2$ for nickel.

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2. Experimental method and results

The resistivity and the absolute thermoelectric power have been measured as functions of temperature, between the liquidus and 1150 °C. The measurements began with the indium–nickel eutectic binary alloy, composed of 46 at.% In and 54 at.% Ni. We added manganese and indium in order to maintain a constant ratio of indium to the transition metals. The measurements were limited to a maximum of 50 at.% of manganese because of the chemical reactivity of manganese with silica and the electrodes at high temperatures. The lowest temperature of the resistivity curves presented in figure 1 corresponds to the liquidus of the ternary alloy. It has been determined from the change of slope of the resistivity observed when decreasing the temperature. With an estimated accuracy of about ± 10 °C, the values obtained for the liquidus are: 936 °C for $x = 0$; 972 °C for $x = 0.1$; 1014 °C for $x = 0.2$; 1049 °C for $x = 0.3$; 1082 °C for $x = 0.4$; and 1108 °C for $x = 0.5$. The measurements of the resistivity and of the absolute thermopower were obtained together, using an automated device described by Vinckel [5] and a quartz cell fitted with tungsten and tungsten/rhenium 26% electrodes. Further experimental details have been given by Auchet and Terzieff [6] and by Gasser [7]. The accuracies are estimated to be: 0.2% for the electrical resistivity; $0.3 \mu\text{V K}^{-1}$ for the thermopower; and 0.5% for the atomic concentration.

In figure 1 we have plotted the experimental resistivity versus temperature at different manganese concentrations. See also figure 2. It is found that, unexpectedly, the resistivity of the $\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$ ternary alloy at 1120 °C decreases on alloying with manganese until a value of the concentration of $x = 0.4$ is reached. The resistivity decreases non-linearly with temperature, as is sometimes found for alloys. We can observe that the temperature coefficient is at its most negative at $x = 0.3$, then it increases again. The resistivity-versus-concentration minimum is obtained for $x = 0.4$; above this, the resistivity increases with manganese concentration and with temperature. This indicates a new phenomenon; indeed the

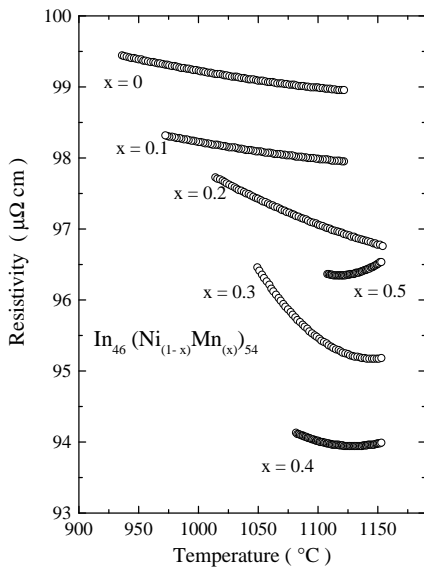


Figure 1. Experimental electrical resistivities of liquid $\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$ alloys as functions of temperature.

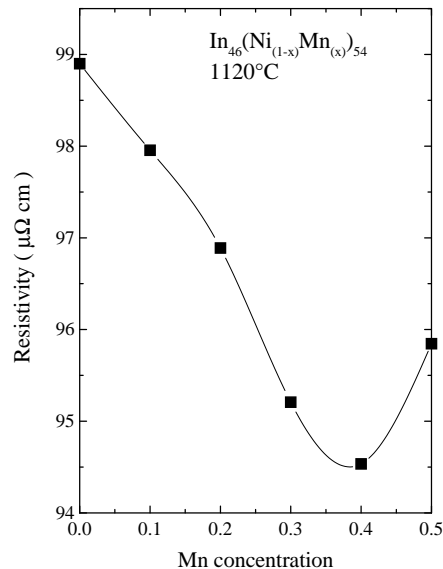


Figure 2. The electrical resistivity isotherm of the liquid $\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$ alloys at 1120 °C versus the manganese concentration x .

resistivity of pure manganese [8] is greater than that of pure nickel. For the binary In–Mn alloy, the resistivity increase with manganese concentration is important, as has been observed by Gasser [1]. The resistivity of In–Ni [3] increases also with the transition metal concentration, but at a lower rate than for In–Mn. The resistivity of the $\text{In}_{46}\text{Ni}_{54}$ alloy at 1000°C is $99\ \mu\Omega\ \text{cm}$ while the interpolated resistivity of $\text{In}_{46}\text{Mn}_{54}$ obtained from the measurements made by Gasser [1, 7] is of about $124\ \mu\Omega\ \text{cm}$. It can be clearly seen that, surprisingly, the variation of the resistivity with the Mn concentration is in the opposite direction to what would be expected. As far as we are aware, this phenomenon is very rare and has not been observed before. As the transition metals are considered to be monovalent, we did not expect that the substitution of manganese for nickel would cause such variations. This confirms that the behaviour of the electronic structure of transition metal alloys is probably more complex than expected.

If one considers the thermoelectric power of the binary $\text{In}_{46}\text{Ni}_{54}$ (figure 3; $x = 0$), one can observe that it is very strongly negative. The thermopower increases with Mn addition. Over the whole temperature range the ATP is non-linear and decreases with temperature until 30 at.% Mn is reached. The alloys at 40 and 50 at.% Mn are practically temperature independent. At the limit of the accuracy of our measurements we note a change of the concavity between 30 and 40 at.% Mn.

We have reported in figure 4 the thermopower of $\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$ ternary alloy as a function of the manganese concentration at constant indium concentration at 1120°C . The thermoelectric power is negative and increases over the whole concentration range from a negative value of $-30\ \mu\text{V}\ \text{K}^{-1}$ to a less negative value of $-5\ \mu\text{V}\ \text{K}^{-1}$ at 50 at.% manganese. It probably continues to increase; indeed Halim [9] obtained an interpolated positive thermopower of $+5.9\ \mu\text{V}\ \text{K}^{-1}$ for the binary $\text{In}_{46}\text{Mn}_{54}$.

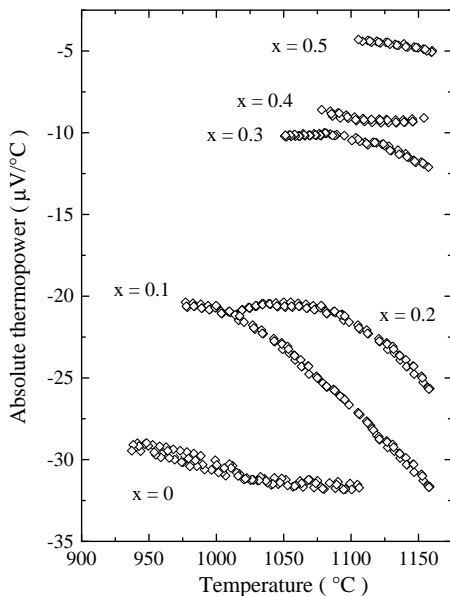


Figure 3. Experimental absolute thermoelectric powers of liquid $\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$ alloys as functions of temperature.

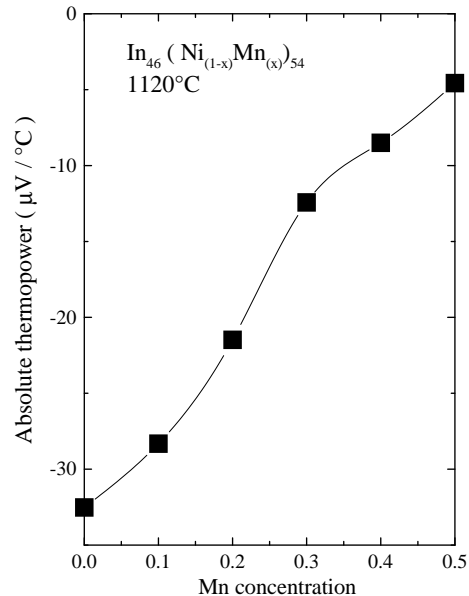


Figure 4. The absolute thermopower isotherm of the liquid $\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$ alloys at 1120°C versus the Mn concentration x .

3. Discussion

In the usual Faber–Ziman representation [10], the electrical resistivity and the thermoelectric power of the metals may be written in the form

$$\rho(E) = \frac{3\pi^2 m_e^2 \Omega_0}{4e^2 \hbar^3 k^6} \int_0^{2k} a(q) |t(q, E)|^2 q^3 dq. \quad (1)$$

The thermopower is given at the temperature T_K by the Mott formula:

$$Q(E) = -\frac{3\pi^2 k_B^2 T_K}{3|e|E} \chi \quad (2)$$

where k_B is the Boltzmann constant. The dimensionless thermoelectric parameter χ is given by

$$\chi = -\left(\frac{d \ln \rho(E)}{d \ln(E)} \right). \quad (3)$$

The resistivity integral, the thermopower and the thermoelectric parameter have to be taken at the Fermi energy $E = E_F$ and at the wave vector $k = k_F$ to be compared to the experimental value.

The electronic transport properties of ternary alloys can be calculated by using the extended Faber–Ziman formalism with three t -matrices and six partial structure factors. To our knowledge, there have been no experimental determinations of partial structure factors for ternary liquid alloys. Saadeddine *et al* [11] have developed a calculation based on a multicomponent hard-sphere interatomic potential corrected by a square well. It has been successfully used to explain the prepeak of the experimental aluminium–nickel–silicon total structure factor.

One of us [7] has shown that whether one uses the experimental or the hard-sphere structure factor for liquid metals does not have a great influence on the resistivity. This can be understood if one compares the integrands of the resistivity of germanium which have been plotted in figure 16 of a paper by Gasser *et al* [12]. For instance the resistivity of a metal like germanium differs by not more than 20%, whereas the experimental and hard-sphere structure factors are very different. It has also been shown [13] for alloys that using the experimental silver–germanium partial structure factor in place of the hard-sphere one does not change the calculated resistivity by more than 20% even if the experimental partial structure factors are very different from the calculated ones. These conclusions may not be exact for non-metallic alloys; indeed all of these examples are taken in the metallic regime.

For the In–Ni–Mn ternary alloy, the structure factors of pure manganese and nickel are not very different. They are hard-sphere-like, following table 3.1 of Waseda's book [15]. The positions of their main peaks do not differ by more than 10%. The variation of the position of $2k_F$ is not greater than 3% in the Dreirach *et al* [14] approach (also described in section 8.3.b of Waseda's book [15]) if one substitutes 40 at.% of manganese for 40 at.% of the nickel content. Thus the structure factor effects alone cannot explain the decrease of the resistivity if x is varied from 0 to 0.4 in the $\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$ alloy.

In the calculations of the electronic transport properties (using formulae (1), (2) and (3)), the crucial point is the determination of the Fermi energy. Different methods have been used to calculate the Fermi energy, following either the approach of Dreirach *et al* [14] or that of Esposito and Ehrenreich [16]. Within Dreirach's model, the parameter to be determined is the bottom of the conduction band E_B , which is referred to as the muffin-tin zero and has been

calculated from the Ziman [10] formula as follows:

$$E_B = -\frac{4\pi}{\Omega_0 k_0} \left\{ \cot \eta_0 - \frac{n_0(k_0, R_{MT})}{j_0(k_0, R_{MT})} \left(\frac{j_0(0)}{j_0(k_0, R_{MT})} \right)^2 \right\}. \quad (4)$$

j_0 and n_0 are Bessel functions. Furthermore, Dreirach *et al* [14] uses a free-electron density of states taking into account only the s band of the transition metal. In the work of Esposito and Ehrenreich [16] the d electrons are taken into account in the band structure and the bottom of the band is always fixed at the muffin-tin-zero potential. The parameter N_c (the effective number of conduction electrons) is introduced and will also be used in this work. The details of how the resistivity and the thermopower can be calculated as functions of energy may be found in the publication of Vinckel *et al* [17] describing the transport properties of liquid silver–gallium alloys. Recent improvements are given in a paper by Makradi *et al* [18]. Similar calculations for nickel and nickel alloys are to be found in [4]. Within that work, it was argued that the electronic structure with two s electrons was the most suitable for describing the resistivity, the thermopower, and the temperature dependence of the resistivity of pure nickel and of the In–Ni alloys. For this reason the subsequent discussion bears only on the electronic structures $3d^8 4s^2$ for nickel and $3d^5 4s^2$ for manganese.

We present in figures 5 and 6 resistivities and the thermopowers of liquid manganese as functions of energy following equations (1) and (2). The energy is not an independent variable and is related to the wave vector k by

$$E = \frac{\hbar^2 k^2}{2m} + E_B. \quad (5)$$

Thus, for each value of E_B , we have curves showing the resistivity and the thermopower versus energy. The different methods described previously have been used to determine the Fermi energy E_F and the effective number of conduction electrons N_c . All of the results are reported in table 1, and the arrows in figures 5 and 6 indicate the different Fermi energies. E_{F1} is calculated

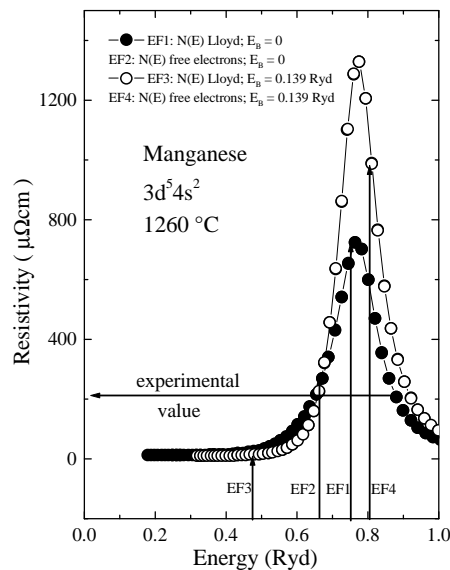


Figure 5. Energy-dependent resistivities of liquid manganese with the $3d^5 4s^2$ electronic structure.

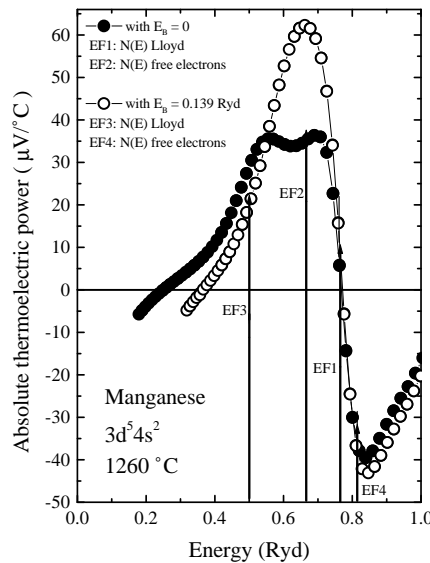


Figure 6. Energy-dependent thermopowers of liquid manganese with the $3d^5 4s^2$ electronic structure.

using $E_B = 0$ and the density-of-states formula of Lloyd [19] (the Esposito approach). E_{F2} is obtained with a free-electron density of states, the number of conduction electrons equal to two (electronic structure $3d^5 4s^2$) and $E_B = 0$ (the simplified Dreirach approach). E_{F3} is determined by combining the Esposito and Dreirach approaches: with $E_B \neq 0$ calculated using the Ziman [10] expression (formula (4)), with the Lloyd density of states and seven $s + d$ electrons. E_{F4} is determined with two $4s$ conduction electrons, $E_B \neq 0$ and a free-electron density of states (the Dreirach approach). The resonance is obtained at 0.76 Ryd (figure 5). The values of E_{F2} and E_{F3} are below the resonance energy. These Fermi energies correspond to effective numbers of conduction electrons respectively equal to 2.00 and 0.77 electrons per atom. The Fermi energies E_{F1} and E_{F4} are respectively near and above the resonance energy. Only E_{F2} gives a value near the experimental resistivity [8]. The experimental thermopower of liquid manganese has not yet been measured to our knowledge due to its reactivity with the container and the electrodes (liquid manganese at 1250 °C dissolves all metals apart from tungsten), but the extrapolation of the data for In–Mn and Sn–Mn indicates a positive value. The thermopower is positive when the resistivity increases with energy and is negative when it decreases. All of the determinations of the Fermi energy correspond to a positive thermopower (except that of E_{F4}). It can be seen that knowledge of both the resistivity and the thermopower is necessary to obtain information on the electronic structure of manganese.

Table 1. The Fermi energy (E_F), bottom of the band (E_B), effective number of conduction electrons (N_c) and experimental and calculated resistivities and thermopowers for liquid manganese obtained using the Esposito [16] and Dreirach [14] procedures.

Mn 3d ⁵ 4s ² 1260 °C	E_F (Ryd)	E_B (Ryd)	N_c	ρ_{exp} ($\mu\Omega$ cm)	ρ_{cal} ($\mu\Omega$ cm)	Q_{exp} ($\mu\text{V K}^{-1}$)	Q_{cal} ($\mu\text{V K}^{-1}$)
$E_B = 0$ $N(E)$, Lloyd	$E_{F1} = 0.756$	0	2.38	200 [8]	707	?	12.5
$E_B = 0$ $N(E)$, free electron	$E_{F2} = 0.672$	0	2		273		35.6
$E_B = 0.139$ $N(E)$, Lloyd	$E_{F3} = 0.496$	0.139	0.77		16		19.6
$E_B = 0.139$ $N(E)$, free electron	$E_{F4} = 0.811$	0.139	2		978		−37

We will now try to interpret our results for the alloys qualitatively. In all of our calculations we have used the Slater [20] approximation for the exchange contribution.

To our knowledge there have been no calculations of the atomic potentials in binary and ternary liquid alloys. It was shown previously for binary alloys [14, 17] that one can obtain a reasonable agreement, conserving the atomic potentials of the pure metals in the Faber–Ziman formalism, if one takes into account the variation of the Fermi energy with composition. The same reasoning can be used to explain the transport properties of the ternary alloy.

In the framework of this formalism, we are able to explain the behaviour of the resistivity (figure 7) and of the absolute thermoelectric power (figure 8) of this system by means of a simple discussion illustrated in figures 7 and 8. For this, it is necessary to plot the resistivity and the thermopower as functions of the energy for the pure transition metals (the resistivity of indium versus energy is nearly constant in the energy domain of interest). The resistivity of nickel versus energy (figure 7) passes through a peak at 0.45 Ryd. The resonance of manganese

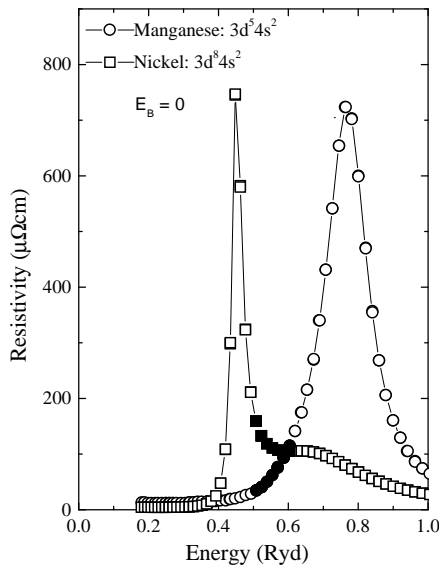


Figure 7. The nickel and manganese resistivities as functions of energy. The full squares and circles indicate the regions where we expect the Fermi energy of the ternary alloy to be found.

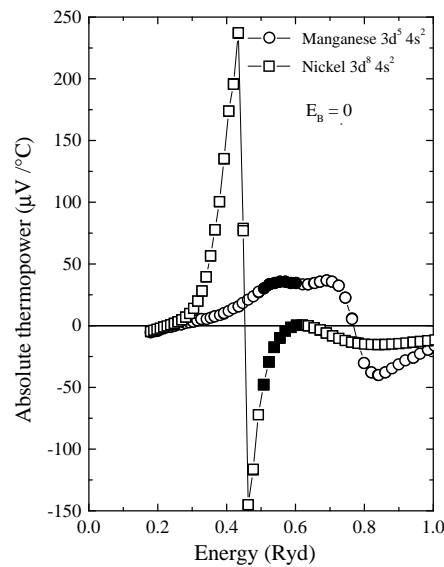


Figure 8. The nickel and manganese thermopowers as functions of energy. The full squares and circles have the same meaning as for figure 7.

is situated at 0.76 Ryd (figure 7). We can consider the Fermi energy at 46 at.% of indium to be located between the resonance energy of nickel and that of manganese. When the manganese concentration increases, the Fermi energy of the alloy increases (solid points in figure 7) and the nickel contribution to the resistivity (weighted by the atomic concentrations) decreases (figure 7) because this energy is located on the right-hand side of the nickel resonance peak. The resistivity begins to increase when the contribution of manganese becomes predominant. This scheme qualitatively explains the unexpected decrease of the resistivity of the ternary alloy very well.

As regards the thermoelectric power (figure 8), the ATP of nickel is negative. The Fermi energy of manganese is higher than that of nickel. It can reasonably be expected to be found between 0.50 and 0.60 Ryd, following the expected experimental transport properties. The addition of manganese to the $\text{In}_{46}\text{Ni}_{54}$ binary alloy increases both the nickel and the manganese contributions to the ATP when the energy increases, as can be observed in figure 8.

4. Conclusions

The behaviour of the resistivity and of the absolute thermopower of $\text{In}_{46}(\text{Ni}_{1-x}\text{Mn}_x)_{54}$ ternary alloy is at first sight surprising. The resistivity decreases with manganese concentration, then increases again, while the absolute thermoelectric power increases as a function of the manganese content.

A qualitative explanation that seems very satisfactory can be given by considering the concentration dependence of the Fermi energy as it is moved from the right-hand side of the nickel resistivity resonance peak to the left-hand side of the manganese resonance peak. The addition of a certain concentration of polyvalent metal (here indium) allows us to shift the Fermi energy to the desired value.

Acknowledgments

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