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Electrical resistivity of Ni–In liquid alloys

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Abstract. The electrical resistivity of liquid $\text{Ni}_x\text{In}_{1-x}$ alloys has been measured as a function of temperature (between the melting point and 1100 °C) and of concentration in 10 at.% steps over the whole phase diagram. The concentration dependence of the resistivity shows a maximum at about 60 at.% nickel. In the neighbourhood of this concentration, the temperature dependence ($d\rho/dT$) changes sign. We have interpreted semi-quantitatively our experimental results using the extended Faber–Ziman theory within the t matrix formalism.

1. Introduction

In simple 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 3d metals are alloyed, the situation is less clear because of the presence of d electrons. This can bring important modifications, an increase in the resistivity for example. The main purpose of this work is to examine the effects of the alloying of nickel (which has a nearly full 3d band) on the resistivity of indium, which has a valency $Z = 3$. After recalling briefly the formalism and the experimental technique used, we present and discuss the electrical resistivity isotherm of the Ni–In system.

The theoretical interpretation is based on Ziman's [1] theory (for pure metals) extended to normal metal alloys by Faber and Ziman [2]. This theory has been used for pure noble metals by Evans *et al* [3] and for transition metal alloys (extended Faber–Ziman theory) by Dreirach *et al* [4]. Some calculations on rare earth metals have been performed by Delley and Beck [5]. Recently Vinckel *et al* [6] performed an energy dependent calculation of liquid silver–gallium alloys by a numerical derivation of the resistivity versus electron energy.

In this work we calculated the resistivity using the formula recalled by Vinckel *et al* [6]. The experimental density is taken from Crawley [7] while the hard-sphere packing fraction is given by Waseda [8]. The input parameters for alloys are deduced from the pure metals parameters using a linear combination with concentration.

2. Experimental method

The electrical resistivity was measured using a four-probe technique on metals having 99.999% purity. In this work, we used a quartz cell fitted with tungsten electrodes, identical to that described by Benazzi *et al* [9]. Further experimental details have been described by Gasser [10]. One important advantage of this cell is the possibility of changing the composition of the alloy during the experiment. Our attention was focused on the possibility of reactions at high nickel concentration between nickel and the tungsten electrode wires.

3. Experimental results

We plot the measured resistivity versus temperature for Ni–In in figure 1. For this alloy the resistivity increases with increasing nickel concentration. A maximum is obtained for Ni–In at 60 at.% Ni. We represent in figure 2 the Ni–In electrical resistivity and in figure 3 its temperature coefficient as a function of nickel concentration at 1000 °C. The resistivity does not depend linearly on the temperature (figure 1). The experimental data have been fitted by a second-order polynomial law (with a correlation factor better than 99.9987% for all concentrations). The coefficients are reported in table 1. As can be seen in figure 2 the resistivity of Ni–In has a maximum of 100 $\mu\Omega$ cm at about 60 at.% Ni. A minimum of the temperature coefficient is observed in figure 3 and is shifted to a value of about 40 at.% Ni.

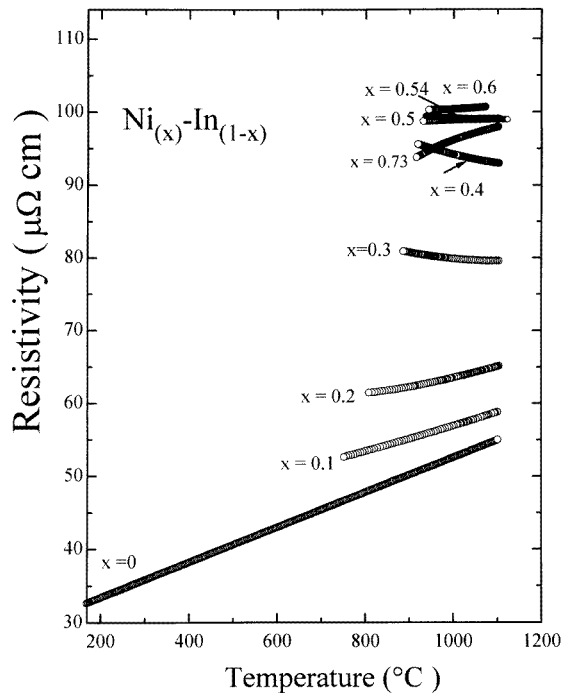


Figure 1. Resistivity of $\text{Ni}_x\text{In}_{1-x}$ alloys between the liquidus and 1100 °C.

4. Discussion

Due to important experimental difficulties only a few measurements are available for liquid transition metal–normal metal alloys (TM–NM). Some of them have been determined at ETH Zürich: Fe–Ge, Co–Ge and Mn–Ge alloys [11]. Others have been measured at Metz, such as Mn–In, Mn–Sn and Mn–Sb alloys [12]. Work has been done at Niigata on dilute TM (between 2 and 6 at.%) in polyvalent metals. Tamaki [13] presents the resistivity of tin–TM alloys, while Ohno *et al* [14] describe antimony–TM alloys up to temperatures of about 900 °C. We observed like Güntherodt and Künzi [11] and Gasser and Kleim [12] a maximum of the resistivity and a minimum of its temperature coefficient (which becomes negative). This minimum is qualitatively understood in the extended Faber–Ziman

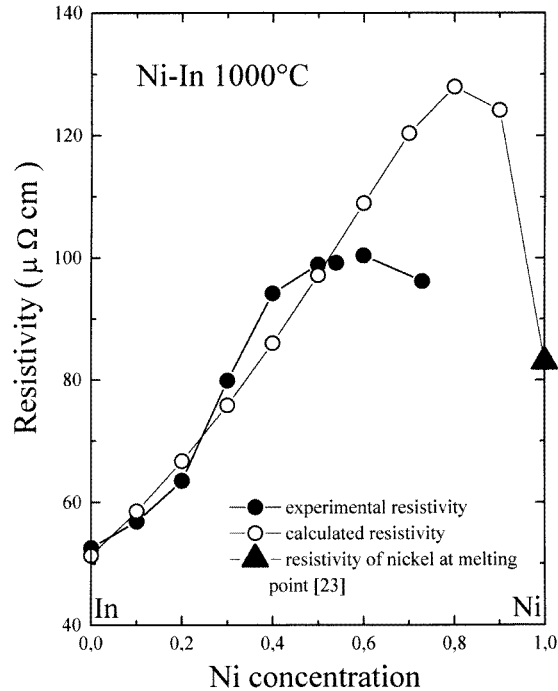


Figure 2. The isotherm of the resistivity of Ni–In at 1000 °C.

Table 1. Coefficients of the least-squares fit to the electrical resistivity of liquid alloys for $\text{Ni}_x\text{In}_{1-x}$ by $\rho = a_0 + a_1T + a_2T^2$: T is in degrees Celsius and ρ in $\mu\Omega$ cm.

| x | a_0 | $a_1 \times 10^3$ | $a_2 \times 10^6$ |
|------|--------|-------------------|-------------------|
| 0 | 28.67 | 23.92 | — |
| 0.1 | 43.67 | 8.059 | 5.19 |
| 0.2 | 66.53 | −20.22 | 17.22 |
| 0.3 | 113.55 | −61.34 | 27.71 |
| 0.4 | 138.58 | −73.85 | 29.49 |
| 0.5 | 90.77 | 14.44 | −6.29 |
| 0.54 | 108.04 | −14.64 | 5.83 |
| 0.6 | 109.64 | −21.29 | 12.061 |
| 0.73 | 17.39 | 135.15 | −56.33 |

theory and is obtained when the mean number of conduction electrons is of about 1.8 electrons/atom. *This indicates clearly that nickel behaves as a monovalent metal in the Ni–In alloys.* The maximum of the resistivity versus concentration curve is obtained a little above the mean valency of 2.1. This shift can be observed in the results of both Güntherodt and Künzi [11] and Gasser and Kleim [12] papers, but has not been discussed in these papers.

The resistivity of a liquid metal can be written $\rho \propto (1/k_F^6) \int_0^{2k_F} a(q)t^2(q)q^3 dq$, where $a(q)$ is the structure factor and $t^2(q)$ is the square of the t matrix. In the case of an alloy the integrand is simply a concentration weighted linear combination of partial structure factors and form factors [6]. Of course the limit of integration $2k_F$ varies with the mean valency

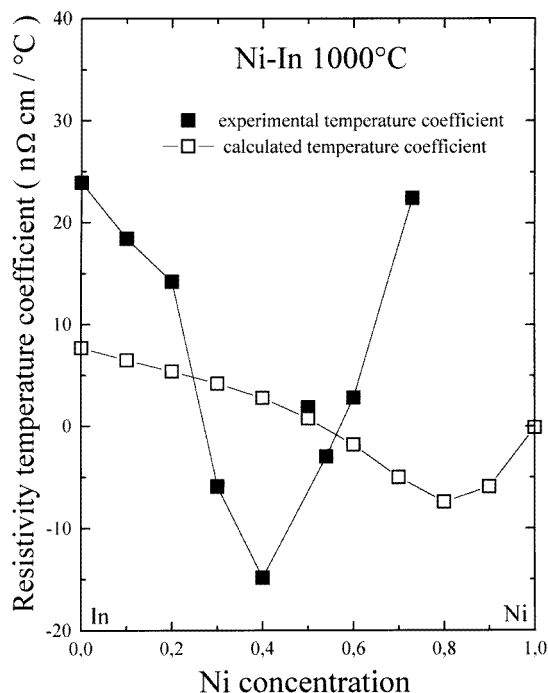


Figure 3. The isotherm of the temperature coefficient of the resistivity of Ni–In at 1000 °C.

of the alloys. A typical shape of the structure factors can be seen in Enderby's review article [15]. The shape of the form factor can be seen in the article by Lee and Lichter [16] in the same book. If we take the product $a(q)t^2(q)$ equal to one, the resistivity is inversely proportional to k_F^6 while the integral is proportional to k_F^4 . Thus the resistivity decreases as $1/k_F^2$ with k_F (with valency). The integrand is modulated by the structure factor which presents a maximum at a q vector corresponding to a valency near 1.8 and which becomes lower than one for a valency near $Z = 3$. This explains why the resistivity versus concentration curve must present a maximum for a mean valency below $Z = 3$. The observed value is 2.1 electrons/atom. To explain the shift we must remember that $t^2(q)$ modulates also the integrand and has a node near $0.8 \times 2k_F$ where the integrand is very small.

The temperature coefficient of the resistivity is a complicated function of the atomic volume. To understand it, it is necessary to remember that the density decreases with temperature. The atomic volume Ω_0 increases with increasing T . The Fermi wave vector k_F ($k_F^3 = 3\pi^2 Z/\Omega_0$) decreases with increasing T . As disorder increases (with increasing T) the structure factor tends to unity: this means that the small q value of the structure factor increases and that the first peak decreases, while the first minimum increases again. The prefactor of the resistivity $1/k_F^6$ increases, while the limit of integration $2k_F$ decreases. The integrand has a part which increases (for $Z < 1.2$), a part which decreases (the first peak with $1.2 < Z < 3$) and a part for $Z > 3$ which increases again. The form factor is normed at $-\frac{2}{3}E_F$ for $q = 0$ and decreases with increasing temperature. The integrand is heavily weighted by q^3 . For all these reasons the resistivity has a minimum in the temperature coefficient when $2k_F$ is situated in the first peak of the structure factor.

Sometimes (depending on the weight of the different variations) the temperature coefficient can become negative. The position of the minimum of the temperature coefficient versus concentration lies very near the position of the main peak ($Z \sim 1.8$).

A quantitative theoretical discussion of these kind of curves was first given by Dreirach *et al* [4]. They replace the transition rate given in the Born approximation (with pseudopotentials) by the probability of scattering by a muffin tin potential traduced in the t matrix.

The calculations of Dreirach *et al* [4] were performed in a quasi-crystalline approximation (QCA). Hirita *et al* [17] replaced the QCA approximation by a method given by Mukhopadhyay [18] using the experimental pair distribution function to construct the muffin tin potential. This method was successfully applied to Cu–Mn, Co–Ge, Ge–Mn and Sn–Co alloys and gave surprisingly good results (within 30% accuracy however). The electronic structure for transition metals was always $(3d)^n (4s)^1$, which is questionable. An energy band shift and an effective mass permitted the fairly good fit to be achieved. Esposito and Ehrenreich [19] showed that this approach was not fully consistent for pure liquid metals and obtained (with a consistent calculation) $1130 \mu\Omega \text{ cm}$ for pure liquid iron while Hirita *et al* [17] obtained $182 \mu\Omega \text{ cm}$ (to be compared to an experimental value of $140 \mu\Omega \text{ cm}$). For liquid cobalt Esposito and Ehrenreich [19] obtained $329 \mu\Omega \text{ cm}$, to be compared to $83 \mu\Omega \text{ cm}$ obtained by Hirita *et al* [17] and $115 \mu\Omega \text{ cm}$, which is the experimental value. We do not know of any other transition metal alloy calculation.

In figure 2 we compare our own calculations with the experimental resistivity versus concentration curve at 1000°C . In figure 3 we compare the temperature coefficients. We observe that a resistivity maximum occurs at a higher nickel concentration than in the experimental curve. The temperature coefficient is also shifted to higher nickel concentrations. Hirita *et al* [17] observed also a shift of the theoretical maximum to higher transition metal concentration for both Co–Ge and Co–Sn alloys (but nobody to our knowledge has calculated the temperature coefficient of the resistivity).

The same phenomenon is observed by Dreirach *et al* [4] on Fe–Ge alloys, but these authors did not present a theoretical calculation of the temperature coefficient either.

One cannot use the Faber–Ziman formula because pseudopotentials are not adequate to describe transition metals. The phase shifts of normal metals such as indium, $\eta_0 = 1.0602$, $\eta_1 = 0.7210$, $\eta_2 = 0.1692$ are determined [20] from the Shaw pseudopotential (in the Born approximation). We took the phase shifts of Lautenschläger and Mrosan [21] obtained from muffin tin potentials for nickel: $\eta_0 = -0.578$, $\eta_1 = -0.144$, $\eta_2 = 2.874$. For the polyvalent metals, the scattering is dominated by the η_0 phase shift while for transition metals η_2 plays the same role. We fitted η_0 for indium ($\eta_0 = 0.932$) to obtain the experimental resistivity of the pure metal. For nickel we have adjusted the η_2 phase shift ($\eta_2 = 2.872$).

The present calculations are satisfactory if one considers the crudeness of the hypothesis. The resistivity was calculated with a hard-sphere potential. Earlier calculations on silver–germanium resistivity [22], with both hard-sphere and experimental structure factors, showed that the experimental structure factor has a small influence on the resistivity ($\approx 20\%$ in that case). For TM–NM alloys the situation is not clear, as has been emphasized by Esposito and Ehrenreich [19] for pure transition metals. However their calculations gave a fairly good result for pure nickel. In the case of alloys we have calculated the resistivity by using the phase shifts of pure metals. However the Fermi energy E_F of the transition metal lies near the resonance of the η_2 phase shift (see for example figure 8.8 of Waseda’s book [8]) and alloying influences strongly the position of E_F . Gasser [10] has shown qualitatively that taking into account the variation of E_F on alloying reduces the maximum of the resistivity versus concentration curve. In our case the η_2 phase shift is $\eta_2 = 2.872$ for pure nickel.

Increasing the Fermi energy by adding a trivalent metal (indium) shifts the η_2 phase shift to higher values (near π) which reduces the resistivity. Thus, the maximum is shifted to a concentration which can be predicted by the qualitative explanations given before, i.e. to a value near the middle of the phase diagram as observed experimentally. The same arguments can also be used for the temperature coefficient. Rigorously, the phase shifts have to be recalculated in the alloy, but this is very difficult and has never been done to our knowledge.

In conclusion we have presented some new experimental results on a liquid transition–polyvalent metal alloy. These results can be qualitatively understood in the framework of the extended Faber–Ziman theory, both for the resistivity versus concentration and for its temperature coefficient if the valence of nickel is taken to be equal to one. Improvement of theoretical calculations must be obtained by taking into account the concentration dependence of the phase shifts.

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References

- [1] Ziman J M 1961 *Phil. Mag.* **6** 1013
- [2] Faber T E and Ziman J M 1965 *Phil. Mag.* **11** 153
- [3] Evans R, Greenwood D A and Lloyd P 1971 *Phys. Lett.* **35** A 57
- [4] Dreirach O, Evans R, Güntherodt H J and Künzi H U 1972 *J. Phys. F: Met. Phys.* **2** 709
- [5] Delley B and Beck H 1979 *J. Phys. F: Met. Phys.* **9** 3
- [6] Vinckel J, Hugel J and Gasser J G 1966 *Phil. Mag.* **B 73** 231–44
- [7] Crawley A F 1974 *Int. Met. Rev.* **19** 32
- [8] Waseda Y 1980 *The Structure of Non-crystalline Materials* (New York: McGraw Hill) pp 54–5, table 3-1
- [9] Benazzi N, Gasser J G and Tezrieff P 1990 *J. Non-Cryst. Solids* **117/118** 391
- [10] Gasser J G 1982 *Thèse de Doctorat d'Etat* Université de Metz
- [11] Güntherodt H J and Künzi H U 1973 *Phys. Kondens. Materie* **16** 117
- [12] Gasser J G and Kleim R 1977 *Third Int. Conf. on Liquid Metals 1976* ed R Evans and D A Greenwood (Inst. Phys. Conf. Ser. **30**) p 352
- [13] Tamaki S 1968 *J. Phys. Soc.* **25** 6
- [14] Ohno S, Okazaki H and Tamaki S 1973 *J. Phys. Soc.* **35** 4
- [15] Enderby J E 1972 *Liquid Metals* ed S Z Beer (New York: Dekker) ch 14
- [16] Lee D N and Lichter B D 1972 *Liquid Metals* ed S Z Beer (New York: Dekker) ch 3
- [17] Hirita K, Jain Y, Waseda A and Srivastava R 1977 *J. Phys. F: Met. Phys.* **7** 419
- [18] Mukhopadhyay G 1973 *Solid State Commun.* **13** 1623
- [19] Esposito E and Ehrenreich H 1978 *Phys. Rev. B* **18** 3913
- [20] Shaw R W 1968 *PhD Thesis* Stanford University
- [21] Lautenschläger G and Mrosan E 1979 *Phys. Status Solidi b* **96** 183
- [22] Kefif B, Halim H, El Ghemaz M and Gasser J G 1990 *Non-Cryst. Solids* **117/118** 387
- [23] Güntherodt H J, Hauser E, Künzi H U and Müller R 1975 *Phys. Rev. Lett.* **54** A 291