

Electronic structure of 3d transition metal solutes in liquid aluminium

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1998 J. Phys.: Condens. Matter 10 4139

(<http://iopscience.iop.org/0953-8984/10/19/002>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 13:08

Please note that [terms and conditions apply](#).

Electronic structure of 3d transition metal solutes in liquid aluminium

P Terzieff† and J Auchet‡

† Institut für Anorganische Chemie, Universität Wien, Währingerstrasse 42, 1090 Vienna, Austria

‡ Laboratoire de Physique des Liquides et des Interfaces, Université de Metz, 1 Boulevard Arago, 57070 Metz Cédex, France

Received 2 March 1998

Abstract. The changes in the electrical resistivity, the thermoelectric power and the magnetic susceptibility of liquid Al due to the addition of small amounts of Ti, V, Cr, Mn, Fe, Co and Ni (1 at.%) are discussed. The variation of the residual resistivity across the series exhibits a characteristic two-peak shape in contrast to the single peak of the solid state. The analysis of the position and the width of the virtual bound d states and the pronounced increase of the magnetic susceptibility point to a magnetically split band structure in the middle of the series. Impurities of Cr and Mn are indicated to be magnetic. V and Fe are presumably on the borderline, whereas Ti, Co and Ni are definitely nonmagnetic if dissolved in liquid Al.

1. Introduction

For several decades, the influence of impurities on the transport properties of simple host metals has been the subject of intensive theoretical and experimental investigation. It is well established that, due to their particular electronic structure, transition metal impurities give rise to the most dramatic changes. In the recent past, some efforts have been made to elaborate the impact of 3d-metal impurities on the electronic properties of liquid host metals [1–4].

Preceding studies were aimed at the experimental investigation of the electrical resistivity, the thermoelectric power and the magnetic susceptibility of dilute liquid Al–3d alloys. The results indicated that the changes were large for impurities of Cr, Mn and Fe, less pronounced for additions of V and Co and small for Ti and Ni [5–7]. Despite the obvious analogy, there is experimental evidence that their influences might strongly depend on temperature or on whether the host is liquid or solid. In fact, the variation of the resistivity through the series was found to differ in a marked manner from that in solid alloys hinting at differences in the electronic structure of the impurity bands. According to the Friedel–Anderson model [8,9] the differences might be due to different positions of the virtual bound d states with respect to the energy, different band widths, and—if indicated—different degrees of band splitting. Basically, it was shown how the experimental findings can be assigned to one single set of model parameters. However, it also became apparent that the limited experimental precision—in particular that of the thermoelectric power—might introduce severe errors. The marked contributions of Cr and Mn to the magnetic susceptibility [5,10] were assigned to localized impurity moments although the usual temperature dependence left some questions open. It is uncertain whether the extremely large width of the impurity band in AlCr (≈ 10 eV at 1273 K), or the marked

variation of the electronic band structure in AlMn with the temperature (on account of the unusual temperature dependence of the magnetic susceptibility), have real physical background. All in all, the results failed to give an unambiguous overall picture of the entire series. In this paper, a general overview will be presented based on the most reliable quantities. Instead of stressing the details of the individual systems, we will attempt to analyse the basic trends within the series and to gain a better understanding by comparing them with those of the solid state.

2. Experimental details and method

High purity metals were used to prepare alloys with the nominal composition of 1 at.% of Ti, V, Cr, Mn, Fe, Co and Ni. All measurements (electrical resistivity, thermoelectric power, magnetic susceptibility) were performed in suitable alumina crucibles, either under a vacuum or argon atmosphere. The data presented in this paper refer to residual (differential) quantities, i.e. the increments due to the impurities. The experimental accuracies were estimated as 0.5% for the residual resistivity, $0.5 \mu\text{V K}^{-1}$ for the residual thermopower, and at least 5% for the impurity susceptibility. More experimental details and results are reported elsewhere [5–7, 11]. The general reference temperature throughout the paper is 1000 K.

The method of evaluation will be based on the concept of virtual bound d states [8, 9]. In the non-magnetic limit, resonance scattering theory in a first approximation gives the residual resistivity $\Delta\rho$ as

$$\Delta\rho = \frac{10hc}{Ze^2k_f} \frac{\Gamma^2}{(E_d - E_f)^2 + \Gamma^2}. \quad (1)$$

Z is the valency of the host, c the impurity concentration, Γ the half width of the impurity bands and $E_d - E_f$ denotes their position relative to the Fermi energy E_f . The residual thermoelectric power ΔS , in turn, can be deduced from the relation

$$\Delta S \frac{\rho_{Al} + \Delta\rho}{\Delta\rho} = \frac{\pi^2 k_B^2 T}{3e} \left[\frac{2(E_d - E_f)}{(E_d - E_f)^2 + \Gamma^2} - \frac{1}{2E_f} \right] - S_{Al} \quad (2)$$

where ρ_{Al} stands for the resistivity of pure Al, and S_{Al} for the thermoelectric power. The number of d electrons per impurity atom is related to the d-wave phase shift ($Z_d = 10\eta/\pi$) and can be expressed by

$$Z_d = \frac{10}{\pi} \tan^{-1} \left(\frac{\Gamma}{E_d - E_f} \right). \quad (3)$$

The spin susceptibility per mole of impurity atoms, usually related to the electronic density of states, is obtained in the following form which includes the enhancement ε due to exchange interactions:

$$\chi = N_A \mu_B^2 \frac{10}{\pi} \frac{\Gamma}{(E_d - E_f)^2 + \Gamma^2} \varepsilon. \quad (4)$$

The formulae adopted in this paper are not represented in the conventional manner, but they emphasize the direct relationship to the crucial model parameters. The complete formalism including the modifications on account of the magnetic limit (i.e. for the case of a two band structure) is outlined elsewhere [5].

3. Results and discussion

The experimental data and the most relevant model parameters are listed in table 1. The variations of the residual resistivity and the residual thermoelectric power across the 3d series are shown in figures 1 and 2, together with the available literature data on solid alloys [12, 13]. The resistivities of the liquid alloys are by a factor of two to three smaller than those of the solid alloys and seem to follow a more complex trend. The changes in thermoelectric power are also less pronounced in the liquid state, but the characteristic shape is the same.

Table 1. Experimental data and model parameters of dilute liquid Al-3d alloys at 1000 K: residual resistivity $\Delta\rho$, residual thermoelectric power ΔS , impurity susceptibility χ , number of d electrons Z_d , position $E_d - E_f$ and half width Γ of the virtual bound d states.

	$\Delta\rho$ ($\mu\Omega$ cm)	ΔS ($\mu\text{V K}^{-1}$)	χ (10^{-6} cm ³ mol ⁻¹)	χ^a (10^{-6} cm ³ mol ⁻¹)	Z_d	$E_f - E_d$ (eV)	Γ (eV)
Ti	1.84	1.40	—	0	2.04	2.11	1.20
V	2.11	1.14	—	225	2.21	2.10	1.76
Cr	3.95	-0.33	—	590	6.60	-3.74	6.79
Mn	3.23	-0.93	737	1085	7.09	-2.10	2.73
Fe	4.65	-2.63	107	345	6.01	-0.28	0.85
Co	2.57	-1.75	-10	50	7.50	-1.28	1.28
Ni	1.14	-0.78	-35	6	8.44	-2.08	1.11

^a Values at 1363 K taken from [10].

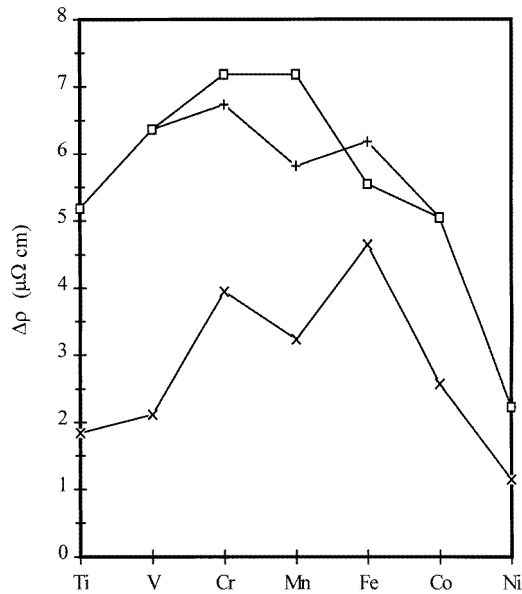


Figure 1. Residual resistivity of dilute Al-3d alloys: \times , liquid alloys (1000 K, this work); \square , $+$, solid alloys (at 4.2 K and 500 K [12]).

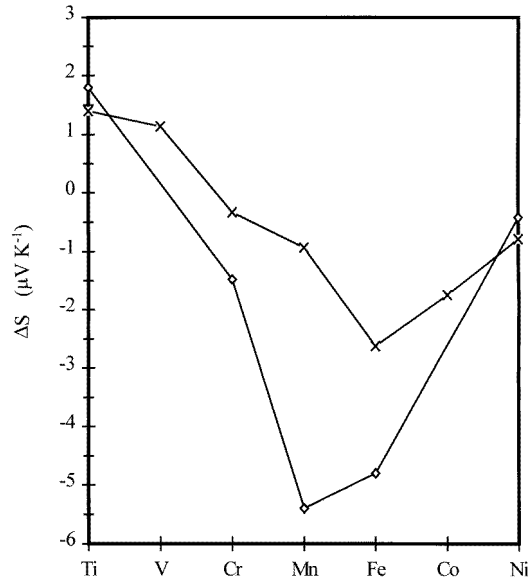


Figure 2. Residual thermoelectric power of dilute Al-3d alloys: ×, liquid alloys (1000 K, this work); ◇, solid alloys (at 293 K [13]).

The magnetic susceptibility was found to vary in a likewise characteristic manner. Figure 3 shows the variation of the deduced impurity susceptibility compared with preceding results on the same series of liquid alloys. Despite the systematic divergence in absolute value our own results confirm the pronounced variation reported by Flynn *et al* [10]. The differences are primarily due (i) to different reference temperatures and (ii) to the final uncertainty in the susceptibility increments due to experimental errors. The extrapolation of our values from 1000 K to 1363 K gives $(1020 \pm 150) \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for Mn and $(190 \pm 120) \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for Fe, in acceptable agreement with the values of Flynn *et al* [10]. The contributions of Co and Ni, according to our findings, are negligible within the experimental error of about $\pm 100 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

The observed increase in resistivity and the changes in the thermoelectric power are, in general, assigned to resonance scattering by the transition metal impurities. The influence on the magnetic susceptibility, on the other hand, is usually assigned to the density of d states at the impurity. (1), (2) and (4) imply that the marked changes in resistivity, thermoelectric power and magnetic susceptibility from one impurity to the other are basically due to the variations of the quantities $E_d - E_f$ and Γ .

According to the early suggestions of Friedel [14] and the experimental evidence from photoemission spectroscopy [15] the positions of the virtual bound states in solid Al are expected to vary from some eV above E_f at the beginning of the series, to some eV below E_f at the end of the series. The analytical expressions given in (1) to (4) suggest an exceptional behaviour around Mn, where the bands are presumably located near E_f (i.e. where $E_d - E_f \approx 0$). The obvious consequences in terms of such a simple picture are that in the middle of the series (i) the residual resistivity passes through a peaked maximum, (ii) the residual thermopower changes sign and (iii) the magnetic susceptibility adopts a maximum value due to a maximum in the density of d states.

The experimental results, as a matter of fact, hint at a more complex situation. In the

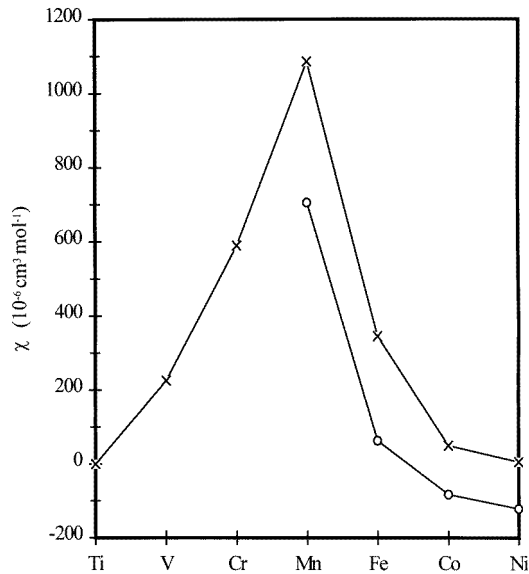


Figure 3. Magnetic susceptibility of 3d impurities in liquid Al at 1000 K (O, this work) and 1363 K (x, [10]).

solid state and at low temperatures, the residual resistivity shows indeed such a simple one-peak structure, but as the temperature increases the residual resistivity of Mn becomes gradually smaller than those of Cr and Fe [12], and finally in the liquid state, the typical double-peak structure prevails (figure 1). The residual thermoelectric power, both in the solid and the liquid, passes through zero between V and Cr, and not at Mn (figure 2). The increase in the magnetic susceptibility, furthermore, is orders of magnitude too large to be assignable to an increased density of states (figure 3).

The quantitative treatment given in previous papers was aimed at the evaluation of the basic model parameters, i.e. the positions and the half widths of the impurity bands [5–7]. Figure 4 gives a summarized representation of the values obtained in the non-magnetic limit of the model by using the formalism outlined in (1)–(4). Except for Cr and Mn our semi-empirical results correlate well with the calculations reported for solid alloys. Both the functional density method of Nieminen and Puska [16] and the first principles calculation of Singh [17] yielded a smooth variation of $E_d - E_f$, roughly between 1.8 eV in AlTi and -1.8 eV in AlNi. In the same sense, the half widths are expected to decrease gradually from 2.2 eV to 0.5 eV. It is obvious that for Cr and Mn neither the position of the d bands (3.7 eV below E_f in AlCr, and 2.1 eV below E_f in AlMn), nor the half widths (6.8 eV in AlCr, and 2.7 eV in AlMn) are compatible with this picture.

It is worthwhile to note that the number of d electrons Z_d obtained for Ti, V, Fe, Co and Ni are very close to the atomic d^n configuration of the elements, while those of Cr and Mn are much higher than expected. This coincides with the observation that the impurity susceptibility passes through a peaked maximum around Mn (figure 3). Figure 4 shows the extremely pronounced variation of the enhancement factor ε which represents the ratio of the experimental impurity susceptibility (taken from [10] so as to have the series at the same reference temperature) to that implied by the model in terms of (4).

All in all, it seems that the non-magnetic description is not representative for the entire

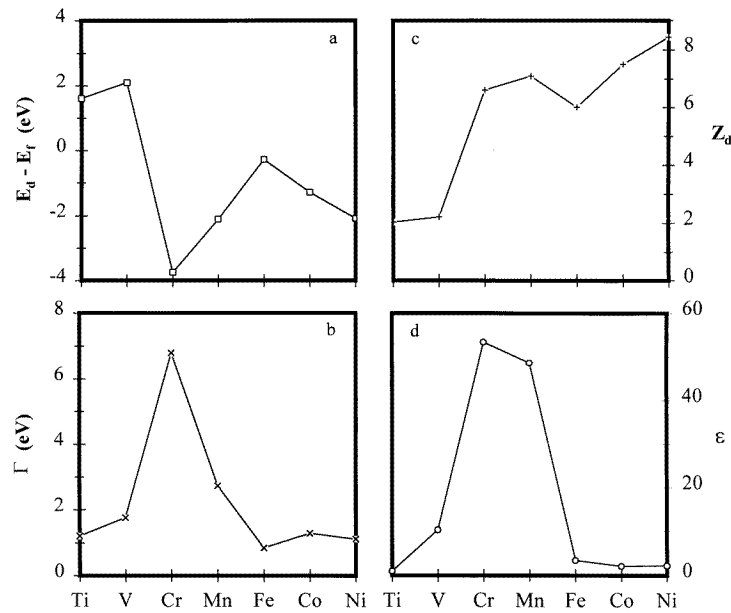


Figure 4. Electronic structure of 3d impurities in liquid Al: (a) the position of the virtual bound d states $E_d - E_f$, (b) their half width Γ , (c) the number of d electrons in the virtual bound states Z_d and (d) the enhancement factor of the magnetic susceptibility ϵ .

series and we may safely assume that at least the exceptional behaviour of Cr and Mn is due to their magnetic character. The extreme enhancement apparent in the middle of the series clearly points to a magnetically split band structure which is responsible for the divergent results obtained from the non-magnetic treatment of Cr and Mn. Additional support is provided by the theoretical calculations for solid alloys which emphasize the exceptional behaviour of Cr and Mn in solid Al. Morinaga *et al* [18] reported a local moment of $2.8 \mu_B$ for Cr, and $2.4 \mu_B$ for Mn, in accordance with the suggestions of Nieminen and Puska [16]. Hence, the resulting magnetic behaviour is expected to be rather that of a classical paramagnet subjected to the interplay between magnetic field and temperature. A first rough estimation tentatively based on Curie's spin-only formula

$$\chi = 4S(S+1) \frac{N_A \mu_B^2}{3k_B T} \quad (5)$$

with $S \approx 1.4$ for Cr, and $S \approx 1.2$ for Mn yields magnetic susceptibilities ($\approx 1200 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for Cr at 1363 K, and $\approx 1300 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for Mn at 1000 K) which are markedly higher than the experimental values (table 1) but of about the correct order of magnitude.

The more elaborate treatment of the experimental results in the magnetic limit of the model (split band structure) was the subject of preceding articles [5–7]. It was shown that all electronic transport properties—including the magnetic susceptibility—could be reproduced with one single set of model parameters. The assumed half widths of 1.9 eV in AlCr and 1.3 eV in AlMn correspond to the trend observed in the series (cf figure 1), and the splitting of the impurity bands (≈ 5 eV for Cr at 1273 K, and ≈ 2 eV for Mn at 1000 K) yield magnetic moments ($1.72 \mu_B$ for Cr, and $1.63 \mu_B$ for Mn) in agreement with the experimental susceptibilities if Curie's law is assumed to hold.

As to the temperature dependence of the magnetic susceptibility [5–7, 10], it has to be emphasized that the magnetic behaviour is not really understood. Both in AlCr and AlMn (and to some extent also in AlFe) the susceptibilities increase markedly with the temperature in contrast to Curie's law as long as the magnetic moments are assumed to be constant. The treatment in terms of the applied model indicates that the splittings of the sub-bands and thus the resulting magnetic moments increase with the temperature thus giving rise to the observed temperature dependence [5].

In view of the experimental uncertainty (in particular that of the residual thermopower) the question is how far the deduced quantities have real physical significance. However, there are strong indications that impurities of Cr and Mn in liquid Al are magnetic, while those of Ti, Co and Ni are obviously non-magnetic; V and Fe are presumably on the borderline between magnetic and non-magnetic. It is difficult to obtain further evidence from the experimental side since the investigation of residual quantities in dilute liquid metals affords extremely high experimental precision. The theoretical work, on the other hand, was up to now primarily concerned with solid alloys at low temperature. Therefore, a theoretical study focused on the liquid state might help to better understand the electronic structure of transition metal impurities in liquid Al.

References

- [1] Nagakawa Y 1959 *J. Phys. Soc. Japan* **14** 1372
- [2] Tamaki S 1968 *J. Phys. Soc. Japan* **25** 379
Tamaki S and Cusack N E 1972 *Phys. Lett.* **41A** 41
- [3] Okada T 1988 *Z. Phys. Chem.* **157** 675
- [4] Ohno S 1977 *J. Phys. Soc. Japan* **42** 194
Ohno S 1977 *J. Phys. Soc. Japan* **53** 1459
Ohno S, Nomoto T and Tamaki S 1976 *J. Phys. Soc. Japan* **40** 72
- [5] Terzieff P, Aucht J and Bretonnet J L 1993 *J. Phys.: Condens. Matter* **5** 1777
- [6] Aucht J and Terzieff P 1996 *Phys. Chem. Liq.* **31** 135
- [7] Aucht J and Terzieff P 1997 *J. Alloys Compounds* **261** 295
- [8] Friedel J 1962 *J. Physique Radium* **23** 692
Blandin A and Friedel J 1959 *J. Physique Radium* **17** 27
- [9] Anderson P W 1961 *Phys. Rev.* **124** 41
- [10] Flynn C P, Rigney D A and Gardner J A 1967 *Phil. Mag.* **15** 1255
- [11] Aucht J and Bretonnet J L 1990 *Rev. Int. Hautes Temp. Refract.* **26** 181
- [12] Babic E, Krsnik R, Leontic B O, Vucic C and Zoric I 1972 *Solid State Commun.* **10** 691
- [13] Crussard C and Aubertin F 1949 *Revue Mét.* **46** 661
- [14] Friedel J 1956 *Can. J. Phys.* **34** 1190
- [15] Steiner P, Höchst H, Steffen W and Hüfner S 1980 *Z. Phys. B* **38** 191
- [16] Nieminen R M and Puska M 1980 *J. Phys. F: Met. Phys.* **10** L123
- [17] Singh P P 1991 *J. Phys.: Condens. Matter* **3** 3285
- [18] Morinaga M, Nasu S, Adachi H, Saito J and Yukawa N 1991 *J. Phys.: Condens. Matter* **3** 6817