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Electronic properties and magnetic moments in liquid AlMn

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Abstract. The effect of Mn impurities on the electrical resistivity, the thermoelectric power and the magnetic susceptibility of liquid Al has been studied. The experimental results are analysed in terms of the Friedel-Anderson model of localized d states, including both the magnetic and the non-magnetic description. Although, in both limits, different experimental quantities can be represented consistently by one particular set of model parameters, the magnetic description produces the more realistic picture. The magnetically split d levels are characterized by a width of 1.3 eV, an intra-atomic interaction energy of $U + 4J \simeq 6.6$ eV and a temperature-dependent spin number of $0.74 \leq S \leq 0.84$ which is assumed to be responsible for the unusual magnetic behaviour. The attempted interpretation in terms of localized spin fluctuations at the manganese sites similarly yields compatible results with a characteristic temperature of $T_k^{sf} \approx 2000$ K in rough accordance with those deduced for solid AlMn.

1. Introduction

The effect of transition-metal impurities on the electronic properties of simple metals has been the subject of many experimental investigations. From the theoretical point of view the experimental phenomena, particularly those observed in noble-metal-based dilute alloys, seem to be well explained by the virtual bound-state concept proposed by Friedel and co-workers [1] and the theory of Anderson [2] which take account of the s-d mixing between the localized impurity levels and the conduction band of the host metal. The basic parameters of the theory are the width Δ of the virtual bound states, their position $E_d - E_F$, relative to the Fermi level, and the effective interaction energy $U + 4J$ which includes the intra-atomic Coulomb energy U and the exchange interaction J between the d levels. The decisive factor determining whether the impurities are magnetic or non-magnetic is the ratio $(U + 4J)/\pi\Delta$; however, there are also intermediate cases. The transition from one regime to the other can be understood in terms of a Kondo-like spin compensation [3] or, alternatively, in terms of the spin fluctuation theory proposed by Suhl [4], Lederer and Mills [5] and Rivier and Zuckermann [6].

In the past, the close relationship between the model parameters and the magnetic state of the impurity atoms has been one of the incentives for studying systematically the conditions for the formation of localized magnetic moments. A summary of experimental data and their relationships to some of the theoretical concepts is given in the review articles of, among others, Daybell and Steyert [7], Heeger [8], Grüner

and Zawadowski [9] and Rizutto [10]. The major part of the experimental work was concentrated on solid alloys and their behaviours at low temperatures, where the influence of transition-metal impurities may be reflected in well pronounced anomalies such as those due to the Kondo effect. In general, such striking phenomena are not to be expected in liquid host metals; they rather represent the asymptotic high-temperature behaviour. On the other hand, measurements on liquid alloys are not affected by solid state reactions (e.g. precipitation) and provide access to a wider range of compositions and temperatures. In the last 10 years, dilute alloys of low-melting-point metals with 3d transition-metal impurities have been carefully investigated, and the results are, as far as they are comparable, consistent with the findings obtained on solid alloys.

Impurities of Mn are definitely magnetic when dissolved in solid or liquid noble metals [11–13], in divalent hosts such as solid Mg or Zn [13, 14], or even in higher-valent liquid metals such as In, Ga, Sn, Sb, Bi or Te [15–17]. In all these cases the ratio $(U + 4J)/\pi\Delta$ seems to be high enough to account for the appearance of localized magnetic moments on the Mn atom, which makes it even more striking to find in the literature that manganese is 'non-magnetic' in aluminium. According to the early measurements of Vogt [18] and Taylor *et al* [19] the magnetic susceptibility of solid AlMn is highly enhanced but fails to show any temperature dependence. The absence of the typical Curie-like behaviour ($d\chi/dT < 0$) implies a Pauli paramagnetism due to non-magnetic impurities, in obvious agreement with the more recent results of Wheeler [20], Aoki and Ohtsuka [21] and Hedgcock and Li [22], and also with the schematic interpretation given by Friedel and co-workers [1]. For liquid AlMn, Flynn *et al* [23] reported similar high magnetic susceptibilities which even markedly increase with increasing temperature; tentatively, this has been assigned to the thermal expansion of the host metal.

Despite this obviously consistent picture it seems unclear whether Mn impurities are actually non-magnetic in Al, in contrast, for instance, with noble metal hosts. By analysing the systematic variation in the impurity resistivity through the 3d series, Babic *et al* [24] suggested that the difference between noble-metal- and aluminium-based alloys is only a question of temperature scale. Similarly, Kedves *et al* [25] even concluded that aluminium-based alloys correspond rather to the magnetic limit of the Anderson model. This is substantiated by the arguments of Grüner and Zawadowski [26] and the theoretical calculations of Morinaga *et al* [27] and those of Deutz *et al* [28].

Apparently, there are sufficient experimental data and well developed theoretical concepts, but some of the features are still not completely understood. Therefore, it was worthwhile to supplement the data existing primarily for the solid state by additional measurements on liquid alloys. The present study will be focused on the electrical resistivity, the thermoelectric power and the magnetic susceptibility of liquid AlMn alloys. In attempting to find a consistent interpretation of the experimental findings, this paper will represent another contribution to the complex problem of moment formation in dilute Al-based alloys.

2. Experimental details

The data reported in this paper refer to a nominal concentration of 1 at% Mn. All electrical measurements were performed in suitable aluminium oxide containers

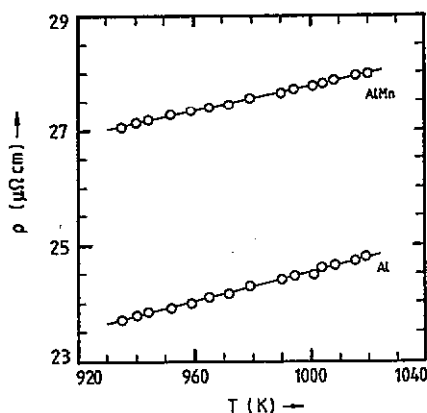


Figure 1. Electrical resistivity of pure liquid Al and liquid AlMn (1 at.% Mn) as function of temperature.

under an inert atmosphere. Thermocouples and electrode wires were protected against chemical reactions with the liquid alloy by massive graphite plugs. The resistivity was determined by the four-point probe technique using an aluminium oxide capillary arranged in a horizontal position and calibrated at room temperature with pure mercury. The thermoelectric power was determined from the slope of the thermoelectric EMF versus ΔT curve, evaluated in the range of small temperature gradients.

The magnetic susceptibilities were measured on a classical Faraday-type balance using aluminium oxide crucibles sealed in quartz as sample containers. At room temperature, different fields were applied so as to identify ferromagnetic contaminations (oxides, etc) by their field strength dependence. The numerical values quoted throughout the paper are corrected by extrapolation to infinite field strength.

This paper is the first part of a systematic study on dilute AlX alloys ($X \equiv \text{Mn, Fe, Co, Ni}$); a more detailed description of the experimental techniques and a critical comparison with the data in the literature on pure liquid aluminium will be given in a forthcoming paper [29]. The discussion will be focused primarily on the residual quantities, i.e. on the differences between the host and the dilute alloy: $\Delta\rho = \rho_{\text{AlMn}} - \rho_{\text{Al}}$ and $\Delta Q = Q_{\text{AlMn}} - Q_{\text{Al}}$; the contribution χ_{Mn}^m of the impurity atoms to the magnetic susceptibility was deduced from the relation

$$\chi_{\text{AlMn}}^m = c\chi_{\text{Mn}}^m + (1 - c)\chi_{\text{Al}}^m. \quad (1)$$

χ_{Al}^m and χ_{AlMn}^m are the experimentally determined molar quantities, and c refers to the impurity concentration.

3. Results

The variation in the electrical resistivity with the temperature was found to be strictly linear up to about 1300 K, for both the pure host and the dilute alloy AlMn containing 1 at.% Mn (figure 1). Accordingly, the resistivities can be expressed by

$$\begin{aligned} \rho_{\text{Al}}(\mu\Omega \text{ cm}) &= 12.047 + 12.497 \times 10^{-3}T \\ \rho_{\text{AlMn}}(\mu\Omega \text{ cm}) &= 16.993 + 10.780 \times 10^{-3}T. \end{aligned} \quad (2)$$

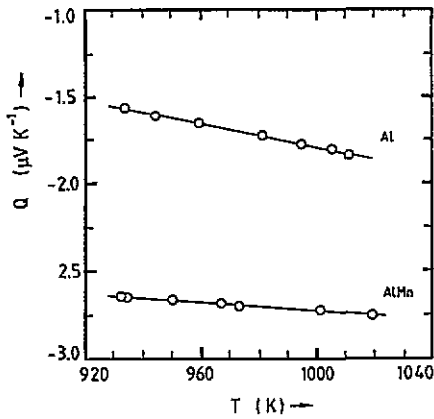


Figure 2. Thermoelectric power of pure liquid Al and liquid AlMn (1 at.% Mn) as function of temperature.

The results of the thermoelectric measurements performed in three different experimental runs are shown in figure 2. Despite some scattering of the data a similar linear relationship between the thermoelectric power and the temperature was indicated within our experimental accuracy:

$$Q_{\text{Al}}(\mu\text{V K}^{-1}) = 1.605 - 3.395 \times 10^{-3}T$$

$$Q_{\text{AlMn}}(\mu\text{V K}^{-1}) = -1.531 - 1.192 \times 10^{-3}T. \quad (3)$$

The values reported by Enderby and Howe [30] are not directly comparable with ours since they refer to higher Mn concentrations (2 and 4 at.% Mn); however, from their data at 1120 K we may deduce a residual thermoelectric power of $-0.55 \mu\text{V K}^{-1}$ which compares well with our value of $-0.67 \mu\text{V K}^{-1}$.

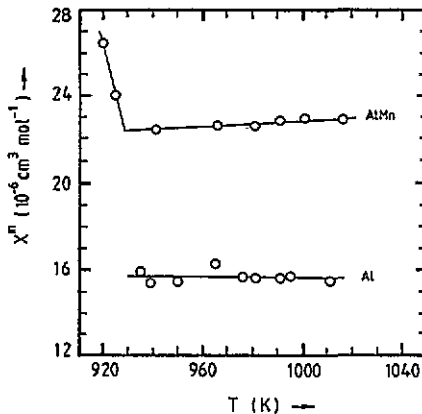


Figure 3. Magnetic susceptibility of pure liquid Al and liquid AlMn (1 at.% Mn) as function of temperature.

As regards the magnetic susceptibility, again a linear variation with the temperature seemed to be indicated. However, unlike the resistivity and the

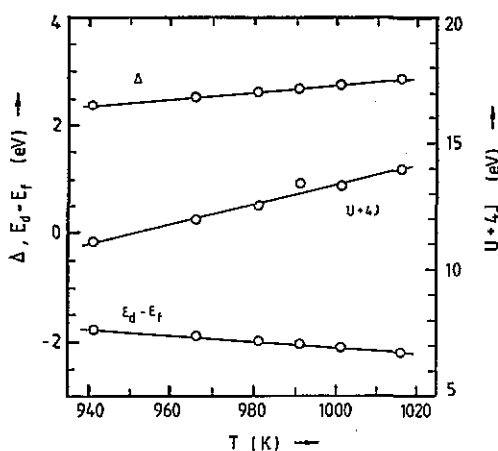


Figure 4. Model parameters of liquid AlMn in the non-magnetic limit of the Friedel-Anderson model as function of temperature: the width Δ of the d states, their position $E_d - E_F$ relative to the Fermi energy and the interaction energy $U + 4J$.

thermoelectric power, the magnetic susceptibility plots for the pure host and the dilute alloy differ in their signs of the slope (figure 3). The discontinuity for AlMn at around 930 K is due to the onset of the solidification process. There are not very many physical reasons for such a linear relationship, but in view of the scattering and the rather small temperature range this approximation is certainly justified. The linear regression yields

$$\begin{aligned}\chi_{\text{Al}}^m (10^{-6} \text{ cm}^3 \text{ mol}^{-1}) &= 16.652 - 0.980 \times 10^{-3} T \\ \chi_{\text{AlMn}}^m (10^{-6} \text{ cm}^3 \text{ mol}^{-1}) &= 15.298 + 7.587 \times 10^{-3} T.\end{aligned}\quad (4)$$

On comparison with the results of Flynn *et al* [23] it has to be emphasized that the impurity susceptibility is highly temperature dependent and thus not directly comparable. If our empirical linear relationships are correct, we may represent the magnetic susceptibility of the Mn impurities in the following form:

$$\chi_{\text{Mn}}^m (10^{-6} \text{ cm}^3 \text{ mol}^{-1}) = -118.75 + 0.8557T. \quad (5)$$

Thus, for the reference temperature of 1363 K we arrive at a value of $1048 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, which is indeed very close to the value of $1085 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ found by Flynn *et al*. As regards the temperature coefficient itself we would expect a value of $2.5 \times 10^{-8} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ for an alloy with 3 at.% Mn which matches well the value of $2.3 \times 10^{-8} \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$ deduced from their paper.

4. Discussion

In the context of the Friedel-Anderson approximation the impurity states are assumed to be of simple Lorentzian form characterized by a width Δ and a certain position $E_d - E_F$ relative to the Fermi level. In the magnetic limit the interaction energy is large compared with the width of the impurity levels, i.e. $(U + 4J) > \pi\Delta$. As a

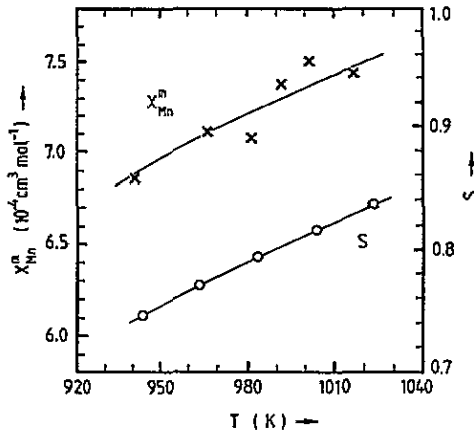


Figure 5. Magnetic susceptibility χ_{Mn}^n and spin S of Mn impurities in liquid AlMn (1 at.% Mn) as function of temperature: x, experimental values; O, calculated in the magnetic limit of the Friedel-Anderson model with $\Delta = 1.29$ eV.

consequence, a split spectrum should be expected and magnetic moments are formed. In general, the model parameters are not exactly known and rough estimates have to be used for practical applications.

In scattering theory the residual resistivity is related to the phase shifts of the partial waves due to the scattering process. Since the impurity states are located near the Fermi level, the resonant phase shift ($l = 2$) certainly gives the major contribution. Consequently, the resistivity can be approximated by the simplified expression already used by Blandin and Friedel [1]:

$$\Delta\rho = (10\hbar c\pi/Z e^2 k_F)(\sin^2 \eta_{\uparrow} + \sin^2 \eta_{\downarrow}). \tag{6}$$

Z is the valency of the host, c is the impurity concentration, and η_{\uparrow} and η_{\downarrow} are the resonant ($l = 2$) phase shifts for the two individual spin directions. Throughout this paper the Fermi vector k_F and the Fermi energy E_F were derived from the appropriate free-electron expressions using the density data of Allen [31].

The residual thermoelectric power can be expressed in terms of the energy derivative of the phase shifts according to

$$Q = (\pi^2 k_B^2 T/3e)(\Delta\rho/\rho_{AlMn}) \{ (1/\Delta\rho)[\partial(\Delta\rho)/\partial E] \}_{E_F} - Q_{Al} \Delta\rho/\rho_{AlMn} \tag{7}$$

$$(1/\Delta\rho)[\partial(\Delta\rho)/\partial E]_{E_F} = (1/\tan \eta_{\uparrow})[\partial\eta_{\uparrow}/\partial E] + (1/\tan \eta_{\downarrow})(\partial\eta_{\downarrow}/\partial E) - \frac{1}{2E_F}. \tag{8}$$

This is similar to the expressions used in a previous paper [32], but adapted for split impurity levels.

4.1. The non-magnetic limit

In this particular case the basic quantities ($\eta = \eta_{\uparrow} = \eta_{\downarrow}$ and $\partial\eta/\partial E = \partial\eta_{\uparrow}/\partial E = \partial\eta_{\downarrow}/\partial E$) could be derived unambiguously at any given temperature. The assignment

to the parameters of the Friedel-Anderson model was achieved via the relations

$$\eta(E_F) = \tan^{-1}[\Delta/(E_d - E_F)] \quad (9)$$

$$(\partial\eta/\partial E)_{E_F} = \Delta/[(E_d - E_F)^2 + \Delta^2]. \quad (10)$$

In the non-magnetic limit the magnetic susceptibility per mole of Mn atoms is directly determined by $N_d(E_F)$, the total density of the d states at the Fermi energy:

$$\chi_{Mn}^m = N_A \mu_B^2 N_d(E_F) \epsilon \quad (11)$$

which, in turn, can be related to the energy derivative of the phase shift by

$$N_d(E_F) = (10/\pi) \left(\frac{\partial\eta}{\partial E} \right)_{E_F}. \quad (12)$$

The spin interactions are accounted for by the fact that the exchange enhancement factor ϵ is coupled to the interaction energy $U + 4J$ via

$$\epsilon = [1 - (U + 4J)N_d(E_F)/10]^{-1}. \quad (13)$$

By making use of our experimental data the phase shifts η , their energy derivatives $\partial\eta/\partial E$, the widths Δ of the virtual levels, their positions $E_d - E_F$, relative to the Fermi energy, the total $N_d(E_F)$ densities of d states, the exchange enhancement factors ϵ and finally the interaction energies $U + 4J$ could be derived in a consistent manner. Tables 1 and 2 summarize the results of our treatment and figure 4 illustrates their systematic variations with temperature. As the characteristic feature, the impurity levels tend to broaden with increasing temperature, while their distance from the Fermi level increases. The total density of d states decreases with the temperature; however, this seems to be outweighed by the rapid increase in the effective interaction energy which is obviously the more crucial factor for the temperature coefficient of the magnetic susceptibility.

Table 1. Characteristic parameters of liquid AlMn in the non-magnetic limit of the Friedel-Anderson model: the resonant phase shifts η , the energy derivatives $(\partial\eta/\partial E)_{E_F}$, the widths Δ of the d states and their relative positions $E_d - E_F$.

T (K)	η	$(\partial\eta/\partial E)_{E_F}$ (eV ⁻¹)	Δ (eV)	$E_d - E_F$ (eV)
941	2.206	0.271	2.392	-1.763
966	2.215	0.253	2.527	-1.898
981	2.221	0.243	2.613	-1.986
991	2.224	0.236	2.674	-2.048
1001	2.228	0.229	2.736	-2.111
1016	2.234	0.220	2.830	-2.210

Some of the quantities deduced in this paper differ significantly from the values reported for solid AlMn. The width of our virtual bound states (about 2.6 eV) is considerably larger than those claimed by Aoki and Ohtsuka [21] (0.2 eV), Hedgcock and Li [22] (0.33 eV), Boato and Vig [33] (about 0.5 eV) and Berthier and Minier

Table 2. Magnetic parameters of liquid AlMn in the non-magnetic limit: the total densities $N_d(E_F)$ of the d states, the total numbers Z_d of d electrons, the impurity susceptibilities χ_{Mn}^{exp} , the exchange enhancement factors ϵ and the intra-atomic interaction energies $U + 4J$.

T (K)	$N_d(E_F)$ (eV^{-1})	Z_d	χ_{Mn}^{exp} ($10^{-4} \text{ cm}^3 \text{ mol}^{-1}$)	ϵ (eV)	$U + 4J$ (eV)
941	0.862	7.02	6.863	24.62	11.12
966	0.805	7.05	7.105	27.30	11.96
981	0.772	7.07	7.066	28.31	12.50
991	0.750	7.08	7.375	31.58	13.40
1001	0.729	7.09	7.494	31.79	13.28
1016	0.699	7.11	7.426	32.88	13.88

Table 3. Characteristic parameters of liquid AlMn in the magnetic limit of the Friedel-Anderson model ($\Delta = 1.29 \text{ eV}$): the spin-up phase shifts η_1 , the spin-down phase shifts η_1 , the relative positions $E_1 - E_F$ and $E_1 - E_F$ of the d states and the densities of states $N_1(E_F)$ and $N_1(E_F)$.

T (K)	η_1	η_1	$E_1 - E_F$ (eV)	$E_1 - E_F$ (eV)	$N_1(E_F)$ (eV^{-1})	$N_1(E_F)$ (eV^{-1})
943	2.563	1.625	-1.975	-0.071	0.738	2.460
963	2.580	1.613	-2.053	-0.055	0.699	2.463
983	2.598	1.602	-2.136	-0.040	0.659	2.465
1003	2.615	1.590	-2.219	-0.026	0.623	2.466
1023	2.632	1.581	-2.313	-0.013	0.586	2.467

Table 4. Magnetic parameters of liquid AlMn in the magnetic limit: the spin-up occupation probabilities $\langle n_1 \rangle$, the spin-down occupation probabilities $\langle n_1 \rangle$, the total numbers of d electrons Z_d , the resulting spins S and the intra-atomic interaction energies $U + 4J$.

T (K)	$\langle n_1 \rangle$	$\langle n_1 \rangle$	Z_d	S	$U + 4J$ (eV)
943	0.816	0.517	6.665	0.746	6.38
963	0.821	0.513	6.674	0.770	6.49
983	0.827	0.510	6.684	0.793	6.61
1003	0.832	0.506	6.692	0.815	6.73
1023	0.838	0.503	6.705	0.837	6.87

[34] (about 0.5 eV). Ratto and Blandin [35] deduced a value of 1–1.5 eV, Hargitai and Corradi [36] found a value of 1.6 eV, and Zlatic and Rivier [37] assumed 1.2 eV to be the most plausible value. Nieminen and Puska [38] calculated a value of 0.8 eV and Mrosan and Lehman [39] found a value of 1.02 eV while, for the non-magnetic case, Deutz *et al* [28] arrived at a value of 1.15 eV, in acceptable agreement with the XPS result of Steiner *et al* [40] (1.3 eV). According to this paper, the virtual bound states are deeper below the Fermi level (about 2 eV) than experimentally observed [40] (about 0.9 eV) or theoretically predicted [28, 38] (0.6 eV).

Owing to the highly increased width of the virtual bound states our density of states (about 0.8 eV^{-1} , deduced from equations (10) and (12)) is obviously one order of magnitude smaller than in solid AlMn (9.4 eV^{-1} [21]), and also smaller than

that reported for liquid AlMn (1.5 eV^{-1} [23]). As a result, we obtain a relatively high enhancement factor ϵ of about 28 and a similarly high interaction energy of $U + 4J \simeq 13 \text{ eV}$. This value differs by an order of magnitude from the value of about 0.5 eV quoted by Aoki and Ohtsuka [21] and is considerably higher than that deduced by Flynn *et al* [23] (about 4 eV). It also exceeds the estimates of Yoshida *et al* [41] and that of Klein and Heeger [42] by a factor of 2.

The total number of d electrons at the impurity site ($Z_d = 10\eta/\pi \simeq 7.1$ electrons/Mn atom) is increased compared with the commonly accepted configuration $d^{n-1}s^1$, indicating the transfer of charge to the impurity atoms. This is not consistent with the result of Berthier and Minier [34] ($Z_d = 5.5$) but correlates well with the total electronic charge calculated by Lautenschläger and Mrosan [43] ($Z_d = 7.49$) and the local valence charge obtained by Deutz *et al* [28] ($Z_d = 7.27$).

All in all, the deduced quantities are of the correct order of magnitude; nevertheless it was of special interest to analyse our experimental data in the magnetic limit. In fact, the quantity $(U + 4J)N_d(E_F)/10 \simeq 1$ signals that the condition for the appearance of spin magnetism is nearly fulfilled.

4.2. The magnetic limit

In this particular case the d levels are assumed to be split into a spin-up and a spin-down component, thus giving rise to the formation of magnetic moments. In the absence of magnetic interactions between the impurity atoms, the magnetic susceptibility is supposed to follow a Curie-like law according to

$$\chi_{\text{Mn}}^m = N_A [(g\mu_B)^2 / 3k_B T] S(S + 1). \quad (14)$$

The spin S per impurity atom is related to the occupation of the split d levels via the simple relation [2]

$$S = 2.5(\langle n_\uparrow \rangle - \langle n_\downarrow \rangle). \quad (15)$$

The occupation numbers $\langle n_\uparrow \rangle$ and $\langle n_\downarrow \rangle$ are determined by the corresponding phase shifts, i.e. $\langle n_\uparrow \rangle = \eta_\uparrow/\pi$ and $\langle n_\downarrow \rangle = \eta_\downarrow/\pi$.

While in the non-magnetic case the model parameters could be calculated directly, a fitting procedure had to be applied for the magnetic case. Strictly, the problem reduces to finding appropriate values of $E_\uparrow - E_F$, $E_\downarrow - E_F$ and Δ which are consistent with the experimental data for $\Delta\rho$ and ΔQ , and which, via equation (14), also reproduce the experimentally observed magnetic susceptibility $\chi_{\text{Mn}}^{\text{exp}}$. The results listed in tables 3 and 4 refer to a constant width Δ of 1.29 eV , which yielded the best fit to the magnetic susceptibility. It is interesting to note that with increasing temperature the spin-up level moves further below E_F (about 2 eV), whereas the half-filled spin-down level remains centred at around E_F , a condition frequently assumed in the literature. The calculations of Deutz *et al* [28], performed for the magnetic case, yielded a sharp majority peak located 1.8 eV below E_F and a less pronounced minority peak at about 0.5 eV above E_F , which has indeed a remarkable resemblance to our findings. Our results are also roughly comparable with the theoretical work of Morinaga *et al* [27] who arrived at a double-hump density of states with one maximum located at about 1.5 eV below and one directly around E_F .

The most remarkable result is the rapid increase in S with increasing temperature which gives, at least in the context of this treatment, an obvious explanation for the

unusual magnetic behaviour of liquid AlMn. Owing to the larger splitting (about 2.1 eV) our magnetic moments ($\mu = 2S\mu_B \simeq 1.6\mu_B$) are smaller than that calculated by Morinaga *et al* [27] ($2.4\mu_B$), that found by Deutz *et al* [28] ($2.5\mu_B$) and also that estimated by Steiner *et al* [44] ($2.2\mu_B$). The total number of d electrons (about 6.7 per Mn atom) is about the same as that obtained for the non-magnetic case; however, concerning the width of the virtual bound states ($\Delta = 1.29$ eV) we observe much better agreement with the data in the literature (cf section 4.1).

The last column of table 4 contains values for the intra-atomic interaction energy $U + 4J$ which is directly related to the splitting of the virtual levels according to [2, 41]

$$E_{\uparrow} - E_{\downarrow} = (\langle n_{\uparrow} \rangle - \langle n_{\downarrow} \rangle)(U + 4J). \quad (16)$$

Compared with the non-magnetic limit they are reduced by a factor of 2 (about 6.6 eV), in excellent accordance with the values suggested by Yoshida *et al* [41] (7–7.5 eV) and Klein and Heeger [42] (6–7 eV).

Once more, it should be emphasized that we compared our results mainly with those obtained for solid alloys and low temperatures. Thus, it would not be surprising to find some systematic differences between AlMn in the liquid and the solid state. Nevertheless, the usefulness of the present treatment seems to be evident.

4.3. Kondo effect

So far, only the two limiting cases, i.e. the non-magnetic and the magnetic regimes of the Friedel–Anderson model, have been taken into consideration. The transition between the two can be thought of in terms of the Kondo effect which, as suggested by Daybell and Steyert [7], should also occur in liquid metals. By analogy to the Friedel–Anderson model, the spin-compensated state ($T \ll T_K$) exhibits a constant, more or less weak Pauli paramagnetism while, in the high-temperature limit ($T \gg T_K$), χ_{Mn}^m should vary as $1/T$, according to Curie's law.

We find it doubtful whether we should identify the actual magnetic behaviour of liquid AlMn with such Pauli paramagnetism, although it is obvious that the magnetic susceptibility can be very sensitive to small changes in the density of states, particularly since $(U + 4J)N_d(E_F)/10 \simeq 1$. On account of the experimental trend, Flynn *et al* [23] assumed that the density of states increases with increasing temperature, but this is in contradiction to our findings for both the non-magnetic and the magnetic case (tables 2 and 3). Since, on the other hand, χ_{Mn}^m also fails to vary with $1/T$, the magnetic behaviour of AlMn seems to be that of a Kondo system with a high Kondo temperature of $T_K < 1000$ K.

Osaka [45] has put forward an analytic expression for the magnetic susceptibility, but, applied to the problem of the very particular temperature dependence of AlMn, it was not possible to reconcile it with our experimental result. However, we may substantiate our rough estimate of the Kondo temperature by applying his formula given for the magnetic susceptibility at T_K :

$$\chi(T_K) = \chi_c[1 - 1/(2S + 1)]. \quad (17)$$

χ_c is the free-spin susceptibility as given by equation (14). If we tentatively assume $S = 1$ as the unreduced impurity spin—this is also compatible with the trend of S with temperature—we arrive at 6.7×10^{-4} cm³ mol⁻¹ for the magnetic susceptibility

which is of the correct magnitude (table 2). Gruber and Gardner [46] deduced the Kondo temperatures of liquid CuAlMn alloys by fitting their susceptibility data in the high-temperature expansion limit. From the systematic variation in T_K with the Al content of the Cu-Al host they estimated $T_K \approx 2000$ K, which also classifies AlMn as a 'high-Kondo-temperature' system. Further evidence of such high 'characteristic' temperatures is provided by numerous other investigations which have been interpreted in terms of the spin fluctuation theory.

4.4. Localized spin fluctuations

An alternative description of nearly magnetic impurities in the Friedel-Anderson model has been given by different workers [4-6] in terms of localized spin fluctuations (LSF). In this picture the boundary between the non-magnetic and the magnetic behaviour of dilute alloys is determined by τ_{sf} , the lifetime of the LSF. Zlatic *et al* [47] have pointed out that, although being based on different concepts, the Kondo and the LSF descriptions yield physically equivalent behaviours. Thus we may safely assume that the Kondo temperature T_K and the characteristic spin fluctuation temperature T_K^{sf} ($k_B T_K^{sf} = \hbar/\tau_{sf}$) have about the same magnitude.

According to the calculations of Rivier and Zlatic [48], the electrical resistivity is expected to vary with T^2 far below T_K^{sf} , with $\ln T$ above T_K^{sf} and linearly with T in the intermediate range.

Liquid AlMn shows in fact such a strict linearity over a wide range of temperatures (figure 1), indicating that the temperatures of our experiments are somewhat below T_K^{sf} in good accordance with our crude estimate of $T_K > 1000$ K. If we relate our empirical relation for the residual resistivity to the expression given in the paper of Rivier and Zlatic [48], namely

$$(1/\Delta\rho_0)[\partial(\Delta\rho)/\partial T] = -[(U + 4J)N_d(E_F)/2.831T_K^{sf}](\pi/10) \quad (18)$$

then we obtain $3.13 \times 10^{-3} \text{ K}^{-1}$ for the term $(U + 4J)N_d(E_F)/T_K^{sf}$ ($\Delta\rho_0$ denotes the residual resistivity extrapolated to 0 K). If we furthermore assume that the temperatures are sufficiently below T_K^{sf} , we may analyse the magnetic susceptibility using the low-temperature formula of Rivier and Zuckermann [6]:

$$\chi_{sf}(g\mu_B)^2(\tau_{sf}/\hbar\pi)[1 - (\pi^2/3\hbar^2)(1 - 3a^2)(\tau_{sf}k_B T)^2]. \quad (19)$$

This expression implies that, if $a > 1/\sqrt{3}$ ($a = (E_F - E_d)/\Delta$), the susceptibility would increase with T^2 . Our value of a deduced for the non-magnetic case (about 0.8) and the XPS result on solid AlMn reported by Steiner *et al* [40] (about 0.8), would indeed explain why χ_{Mn}^m increases with increasing temperature. Applying equation (19) directly to our experimental data we arrive at an apparently higher a of 1.6 ± 0.8 and a spin fluctuation lifetime τ_{sf} of about $(1.9 \pm 0.6) \times 10^{-15}$ s which implies a spin fluctuation Kondo temperature of $T_K^{sf} = 4000 \pm 1200$ K. Together with the value of $(U + 4J)N_d(E_F)/T_K^{sf}$ quoted above, we end up with $(U + 4J)N_d(E_F)/10 = 1.2 \pm 0.4$ which places AlMn indeed very close to the instability limit.

Alternatively, and probably in a more reliable manner, τ_{sf} can also be derived from the slope according to equation (19) provided that a is known. Thus, using the experimentally supported value of $a = 0.8$ we arrive at a higher spin fluctuation lifetime of $(3.8 \pm 0.3) \times 10^{-15}$ s, and a reduced spin fluctuation temperature of 2000 ± 150 K. From these we obtain $(U + 4J)N_d(E_F)/10 = 0.63(\pm 0.05)$ which

compares well with the value of about 0.7 deduced from the density of states given by Aoki and Ohtsuka [21] for solid AlMn ($N_d(E_F) = 9.5 \text{ eV}^{-1}$) and the value of $U + 4J \simeq 7 \text{ eV}$ estimated by Yoshida *et al* [41] and Klein and Heeger [42].

Thus far we have based our consideration on the validity of equation (19); however, although our experimental temperatures were always much lower than the spin fluctuation temperature the condition $T \ll T_K^{\text{sf}}$ was never strictly fulfilled. Moreover, it is not clear whether equation (19) holds for $a \simeq 1$. The expressions given by Hedgcock and Li [22] and Schotte and Schotte [49] are equivalent to equation (19) only for small values of a .

Instead of deducing τ_{sf} from the magnetic susceptibility we may apply the expression of the renormalized spin fluctuation theory put forward by Parton and Zuckermann [50]. Its application to the high-temperature resistivity of solid AlMn predicts a linear temperature dependence of the resistivity which extrapolates to zero at $k_B T = 1.07\hbar/\tau_{\text{sf}}$ [51]. Applied to our data this would imply a lifetime of $\tau_{\text{sf}} \simeq 3 \times 10^{-15} \text{ s}$ and consequently a characteristic temperature of $T_K^{\text{sf}} \simeq 2700 \text{ K}$. This compares roughly with the values of 3100 K and 1500 K deduced in a similar manner from the results of Babic *et al* [52] and Kedves *et al* [25], respectively. Alloul and Launois [53] found the Knight shift to vary inversely with the temperature with a characteristic temperature of about 2000 K, which is the same as the extrapolated estimate of Gruber and Gardner [46].

Daybell and Steyert [7] have emphasized that the experimentally deduced characteristic temperatures are not unique since they may differ from method to method; nevertheless the overall agreement seems to be acceptable. Summarizing all our experimental evidence we can safely assume $2000 \pm 1000 \text{ K}$ to be the most probable value of the spin fluctuation temperature T_K^{sf} .

5. Conclusion

Different theoretical approaches have been applied in order to give a consistent interpretation of the electronic properties of dilute liquid AlMn. The magnetic character of the Mn impurities turned out to be one of the key factors. The two extreme situations—the non-magnetic and the magnetic limit—were elaborated with the help of the Friedel–Anderson model by making use of the experimental resistivities, the thermoelectric power and the magnetic susceptibility. Although the alternative treatments lead to a picture which is consistent with all experimental observations, the magnetic limit yields a more plausible band width (1.29 eV compared with about 2.6 eV) and a more realistic interaction energy $U + 4J$ (about 6.6 eV instead of about 13 eV). Furthermore, the systematic increase in the impurity moment with increasing temperature seems to be an inherent feature of the model whereas in the non-magnetic limit an extremely high enhancement factor (about 28) has to be assumed.

In treating AlMn as intermediate case the Kondo model and/or the equivalent description in terms of the spin fluctuation theory may be applied. Whereas the Kondo model allows only a very crude estimation of the Kondo temperature ($T_K > 1000 \text{ K}$), the concept of LSF is found to be successful in explaining the linear temperature dependence of the residual resistivity, giving a characteristic temperature T_K^{sf} of about 2000 K. Our best estimates of $\tau_{\text{sf}} \simeq 3 \times 10^{-15} \text{ s}$ and $\Delta \simeq 1.3 \text{ eV}$ imply that $\hbar/\Delta\tau_{\text{sf}} \simeq 0.17$, which is about the same as that for solid AlMn [37] (0.12), indicating the existence of LSF [37].

Considering the significance of the quantities deduced, it should be stressed that the impurity contributions were assumed to be additively superimposed on that of the pure host, i.e. eventual perturbations of the neighbourhood around the impurity sites were neglected. This is not self-evident, particularly not in the case of the magnetic susceptibility, where the enhancement of the host susceptibility itself might be affected by the presence of impurities. In addition, throughout this paper, solid state theories have been applied to liquid alloys in a somewhat oversimplified form; therefore some of the results might be only of approximate character. However, we may confidently assume that the trends are correct.

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