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Abstract. The results of an experimental study of the residual resistivity and thermopower of Fe, Co and Ni dilute in liquid Al are presented. Combined with the magnetic susceptibility, our results are found to be consistent with the predictions of the Friedel–Anderson model and are used to determine the parameters of the virtual bound state as well as the exchange–correlation energy between two electrons localized on the site of the impurity.

1. Introduction

Because they are closest to the underlying virtual bound state (VBS) model introduced by Friedel [1] and Anderson [2], the impurity systems of 3d ions in Al have been extensively investigated both from the experimental and the theoretical point of view. In solid state, the VBS parameters have been obtained from a number of measurements such as resistivity [3, 4], thermopower [5, 6], magnetic susceptibility [7] and x-ray photoelectron spectroscopy [8]. In contrast, little has been done on these systems in liquid state. Flynn *et al* [9] have shown that 3d transitional impurities do not give rise to localized magnetic moments in liquid Al. Residual resistivity data are also available [10]. Recently, we have undertaken the measurements of the thermopower of Fe, Co and Ni dissolved in liquid Al. Our experimental results are reported in this paper with the purpose of subjecting to a further check the VBS model, and of deducing the enhancement factor of the core state susceptibility. In the non-magnetic case, the impurity state is characterized by a Lorentzian density of state with width 2Δ at the position E_r near the Fermi energy E_F. The aim of our investigation is to determine the VBS parameters and to confirm the assumption that the width is nearly constant for the studied systems.

2. Experimental results and model

The results both of the residual resistivity and the residual thermopower of liquid alloys Al–Fe, Al–Co and Al–Ni are shown in table 1. Experimental details and full results of resistivity are published elsewhere [10]. The thermopower measurements were carried out by using the small-ΔT method. The liquid metal was contained in an open alumina crucible under an inert atmosphere. The two measurement thermocouples were inserted

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Table 1. Experimental values of the residual resistivity, thermoelectric power and magnetic susceptibility, at 1000 °C. $\rho_{Al} = 28\ \mu\Omega$ cm and $S_{Al} = -2.72\ \mu V\ K^{-1}$ [10]; χ_d is taken from [8].

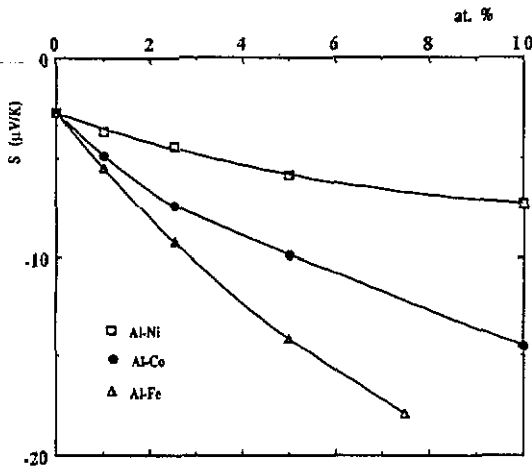| $c = 1$ at.%	$\Delta\rho$ ($\mu\Omega$ cm)	ΔS ($\mu V\ K^{-1}$)	χ_d (cgs 10^6 mol^{-1})
Al–Fe	4.203	−2.76	375
Al–Co	2.512	−2.12	85
Al–Ni	1.233	−0.98	45

Figure 1. Thermoelectric power of liquid alloys of Al with Fe, Co and Ni, at 1000 °C.

into dense graphite plugs to prevent contamination. A description of the method was made in an earlier paper [11]. As shown in figure 1, the thermopower of Al decreases on alloying with transition metals and thermopower isotherms present a quasi-linear variation in the ranges of concentrations studied, at 1000 °C. In the case of Fe and Co, the discard with regard to the linearity is more marked. The quasi-linear behaviour is also observed for liquid systems of Fe, Co and Ni in Sn [12], but it differs from that of transitional impurities in Ge alloys [13].

To analyse our results we used free-electron phase shifts, as did Friedel in his early treatment of this problem. In this model, both the residual resistivity $\Delta\rho$ and the residual thermopower ΔS are governed by the proximity of the Fermi energy E_F to a resonance in the $1 = 2$ phase shift, thus a good approximation for $\Delta\rho$ is

$$\Delta\rho = \rho_{all} - \rho_{Al} \simeq (20\pi\hbar c/Ze^2 k_F) \sin^2 \eta_2(E_F) \tag{1}$$

where c represents the concentration of the impurity in at.%, Z is the valence of the solvent and k_F the Fermi wave-number. It is found that the residual thermopower ΔS is not given by the derivative of the residual resistivity $\Delta\rho$ but is written with the usual relation

$$\Delta S = S_{all} - S_{Al} = \frac{\pi^2 k_B^2 T}{3e} \frac{\Delta\rho}{\rho_{all}} \left[\frac{1}{\Delta\rho} \frac{\partial\Delta\rho}{\partial E} - \frac{1}{\rho_{Al}} \frac{\partial\rho_{Al}}{\partial E} \right]_{E = E_F} \tag{2}$$

Table 2. Virtual bound state parameters for liquid alloys of Al with Fe, Co and Ni.

$c = 1$ at.%	$\eta_2(E_F)$	$(\partial\eta_2/\partial E)_{E_F}$ (eV)	2Δ (eV)	$(E_F - E_r)$ (eV)	$N_d(E_F)$ (eV)$^{-1}$	ε	$\bar{U}_{xc}$ (eV)
Al–Fe	2.027	0.733	2.20	0.54	2.33	5.03	0.34
Al–Co	2.375	0.418	2.30	1.19	1.33	2.00	0.37
Al–Ni	2.634	0.219	2.16	1.94	0.70	2.00	0.71

where

$$S_{Al} = \frac{\pi^2 k_B^2 T}{3e} \frac{1}{\rho_{Al}} \left(\frac{\partial\rho_{Al}}{\partial E} \right)_{E_F} \tag{3}$$

$$\frac{1}{\Delta\rho}\left(\frac{\partial\Delta\rho}{\partial E}\right)_{E_F} \simeq \frac{2}{\tan\eta_2}\left(\frac{\partial\eta_2}{\partial E}\right)_{E_F} - \frac{1}{2E_F}. \tag{4}$$

The residual thermopower depends not only on the phase shift η_2 but also on its derivative with respect to energy. Thus, both the values of η_2 and $\partial\eta_2/\partial E$, at the Fermi level, can be obtained from (1)–(4) as well as from the measured transport properties, namely $\Delta\rho$, ρ_{Al}, ΔS and S_{Al}.

3. Discussion and conclusion

Now, we can afford to give the VBS parameters of d impurities in liquid Al. According to the classical expressions in the theory of scattering, the phase shift $\eta_2(E_F)$ and its energy dependence are written as

$$\eta_2(E_F) = \tan^{-1}[\Delta/(E_r - E_F)] \tag{5}$$

$$(\partial\eta_2/\partial E)_{E_F} = \Delta/[(E_r - E_F)^2 + \Delta^2]. \tag{6}$$

The relevant VBS parameters are shown in table 2. The resonant scattering contribution is clearly dominant; therefore the calculations are quite sensitive to the relative position of the resonance, E_r, to the Fermi level and also its width, 2Δ. The three systems under consideration exhibit a more or less constant width ($2\Delta \sim 2.2$ eV) and a centre of the VBS below E_F. When E_r approaches E_F, going from Ni to Fe, we observe a large residual thermopower as a consequence of the resonant d-state. For 3d impurities in solid Al some information on VBS has been already obtained from experiments and we can compare our results with those from a similar analysis. The thermopower measurements [5] lead to a generally small width: $2\Delta \sim 1$ eV for Fe and 0.54 eV for Mn. According to specific heat [14], the values of 2Δ are quite comparable with those that stem from the thermopower. Small changes are found when the VBS parameters are obtained directly by XPS [8]; the values of 2Δ lie between 1.65 and 1.8 eV. For the sake of comparison, it is still worth quoting the average value of 2Δ (~ 2 eV) for 3d impurities in liquid tin [12].

Using our experimental results of resistivity and thermopower, as well as those of the magnetic susceptibility [9], it is easy to calculate the energy describing the electron

interaction. For 3d transition impurities in liquid Al, the molar paramagnetic susceptibility of core states χ_d is temperature-independent and therefore may be written

$$\chi_d = N_A \mu_B^2 N_d(E_F) \varepsilon \tag{7}$$

where N_A is the Avogadro number, μ_B is the Bohr magneton,

$$N_d(E_F) \ (\simeq (10/\pi)(\partial \eta_2/\partial E)_{E_F})$$

is the density of core states and ε is an enhancement factor given by the following relation

$$\varepsilon = [1 - \bar{U}_{xc} N_d(E_F)]^{-1}. \tag{8}$$

$\bar{U}_{xc}$ is the average exchange and correlation energy arising from the occasional occupation of electron pairs in the incomplete d-shell of an atom. While the non-magnetic state is a stable state when $\bar{U}_{xc} N_d(E_F) < 1$, the susceptibility becomes infinite when the magnetic instability is approached. $\bar{U}_{xc}$ can be approximately separated [15] into the self energy terms U_{xc} and the exchange terms J, such as

$$\bar{U}_{xc} \equiv (U_{xc} + 4J)/5 \tag{9}$$

but, with an average value of 0.6 eV, the exchange terms J responsible for the magnetism in free atoms and ions are only a small contribution to $\bar{U}_{xc}$.

Our results of ε and $\bar{U}_{xc}$ obtained with (7) and (8) are shown in table 2. The values of $\bar{U}_{xc}$ cannot be compared with those of the free atom—more than 5 eV—because of its stringent reduction in the metal caused by the screening and the many-body correlation effects. In contrast, they can be compared to the more precise estimate taking account of the intra-atomic Coulomb correlations and kinetic interatomic correlations. According to Friedel [15], $\bar{U}_{xc}$ should lie in the range 0.5 to 1 eV. For Fe and Co, our values are a little smaller but a more detailed comparison should be non-significant because such an estimate is more appropriate for nearly full or nearly empty bands and a complete study of this problem is still lacking.

A first attempt has been made by Flynn *et al* [9] to determine ε from their magnetic susceptibility experiments, with an assumed value of $\bar{U}_{xc}$ of 0.4 eV for each element of the 3d series in liquid Al. Our results are in good agreement with theirs and, for Fe and Co, they confirm entirely the estimated value of 0.4 eV, while for Ni our result is about double. However, it is worth noting that, from susceptibility and specific heat measurements of Ni in Be, Klein and Heeger [16] found the same value of $\bar{U}_{xc}$ (=0.73 eV) as we did for Ni in Al. As far as can be judged, the comparison of the values of $\bar{U}_{xc}$, in table 2, might indicate that the Fe and Co atoms are screened more drastically than the Ni atoms in liquid Al.

On the other hand, the Fe impurity has both a greater density of states and enhancement factor. Thus, according to the instability criterion one concludes that Fe is more favourable for the formation of a magnetic state than Co or Ni, in liquid Al. There is experimental evidence to suggest that in some systems, e.g. Cr or Mn in Al [17, 18], the effect of fluctuations cannot be ignored. These effects may occur in nearly magnetic alloys containing a quantity of impurities just less than that required to support a local magnetic moment. The presence of impurities causes local composition fluctuations which give rise to localized spin fluctuations [19]. Such fluctuations arise when $\bar{U}_{xc} N_d(E_F)$ is just less than unity and so large spin fluctuations into the magnetic state can appear although the system is not magnetic in the Hartree–Fock sense. With the values of $\bar{U}_{xc}$ observed on the Al–Fe system, we might expect to find some remaining collective spin excitations in that liquid system.

In summary, it appears from our results that the width of the VBS is found to be nearly constant, agreeing fairly well with the prediction of the models and appreciably greater than in solid state. Besides, the analysis of our experimental results provides an estimate of the exchange-correlation energy between two electrons localized on the impurity in the metallic environment. Thus, it encourages us to pursue an experimental study on the 3d transition metals with less than half-filled bands in liquid aluminium.

Acknowledgment

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