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The thermoelectric power and resistivity of liquid Co-Ni

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Abstract. The thermoelectric power, S , and electrical resistivity, ρ , have been measured as functions of concentration, c , for the liquid alloy system Co-Ni. It turns out that both $\rho(c)$ and $S(c)$ follow the theoretical predictions of Evans *et al* (1971 *Phys. Lett.* 35A 57) if a low effective valence (of the order of 0.2) can be assumed. For valencies nearer unity, theory and experiment do not agree.

1. Introduction

In recent years two schemes have been proposed for the calculation of the electronic transport properties of transition metals and their alloys. The essence of the 'Bristol' method (see, for example, Evans *et al* 1971, Dreirach *et al* 1972) is to suppose that the nearly free electron formula for the resistivity ρ and the thermopower S (Ziman 1961) can be applied to liquid transition metals, provided the scattering from a single centre is calculated from the transition matrix:

$$t(k, k') = \frac{-2\pi\hbar^3}{m(2me)^{1/2}} \left(\frac{1}{\Omega_0} \right) \sum_l (2l+1) \sin \eta_l(\epsilon) \exp(i\eta_l(\epsilon)) P_l(\cos \theta).$$

The notation is standard, Ω_0 representing the atomic volume and $\eta_l(\epsilon)$ the l th partial-wave phase shift calculated at energy ϵ . In this model both ρ and S are governed by the proximity of the Fermi energy ϵ_F to a resonance in the $l=2$ phase shift and to a good approximation are given by the relatively simple expressions

$$\rho = \frac{30\pi^3\hbar^3}{m\epsilon_F k_F^2 \Omega_0 e^2} \bar{a} \sin^2 \eta_2(\epsilon_F) = A \bar{a} \sin^2 \eta_2(\epsilon_F) \quad (1)$$

$$S = \frac{\pi^2 k_0^2 T}{3|e|\epsilon_F} \left(-2 + \frac{\epsilon_F}{\bar{a}} \frac{\partial \bar{a}}{\partial \epsilon} \Big|_{\epsilon_F} + 2\epsilon_F \cot \eta_2(\epsilon_F) \frac{\partial \eta_2}{\partial \epsilon} \Big|_{\epsilon_F} \right). \quad (2)$$

The methods used to calculate the Fermi energy ϵ_F , the radius of the Fermi sphere k_F and the phase shifts are discussed in detail by Dreirach *et al* (1972) and by Brown (1973). The liquid structure factor evaluated at a momentum transfer value, q , of $2k_F$ and represented by \bar{a} can be obtained either from experiment (Waseda and Tamaki 1975, Waseda and Ohtani 1975) or from a solution of the Percus-Yevick equation for hard spheres (Ashcroft and Lekner 1966).

A basic objection to the method has, however, been formulated by Mott (1972). He argues that there are two mean free paths in the problem, one associated with the s and p electrons and the other with d electrons. Furthermore, the dominant contribution to

the resistivity comes about, Mott argues, from $s-d$ scattering and depends sensitively on $N_d(\epsilon)$, the d contribution to density of states. The effect of multiple scattering is to make $N_d(\epsilon)$ considerably broader than the single-site d -resonance from which it ultimately derives. Thus whilst the resonance theory in its elementary form may apply to liquid alloys involving an appreciable amount (>25 at. %) of a non-transition metal, it might fail for those cases in which the d -band overlap integral is greater than a critical value (estimated by Mott as about 0.05 eV).

It was to throw further light on the theoretical problems posed by liquid transition metals that the series of experiments reported here were undertaken.

2. Experimental

The idea behind the present study was similar to that developed by Howe and Enderby (1967) who recognized that the difficulties (see §3 below) involved in making a direct comparison between theory and experiment could be avoided by focusing attention on the resistivity and the thermoelectric power of suitably chosen binary alloy systems. The method, which allows S for the alloy to be predicted from the properties of the pure components, works when the Fermi energy, atomic volume and liquid structure factors are concentration independent; it was applied successfully by Howe and Enderby (1967) to liquid Ag–Au.

The system chosen for this study was liquid Co–Ni because (i) the composition range and the evidence from the phase diagram (Hanson 1958) and the structure data (Waseda and Tamaki 1975) strongly favour a substitutional model for a ; (ii) interpolating the data provided by Dreirach *et al* (1972) we find a change in ϵ_F across the composition range of less than 10%; (iii) according to Heine (1967), k_F for Co and Ni are essentially equal.

The experiments were carried out at temperatures of 1500°C in a specially constructed apparatus, the principle of which was briefly described in an earlier communication (Dupree *et al* 1975; a full description of the method will appear elsewhere). The method ensured that the total sample contamination introduced by the tungsten counter electrodes did not exceed about 0.4 at. % in the most unfavourable case and

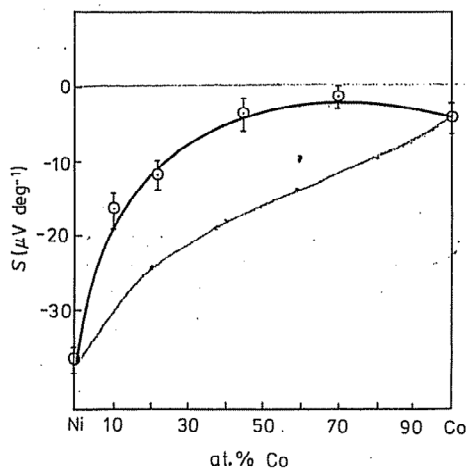


Figure 1. Thermoelectric power for liquid Ni–Co alloys at 1500°C .

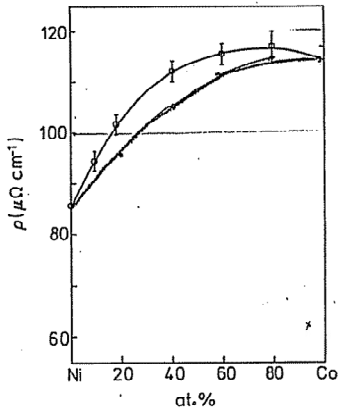


Figure 2. The resistivity for liquid Ni-Co alloys at 1500 °C

tests showed that this level of impurity did not, within experimental error, affect the observed thermoelectric power or resistivity. The basic technique was checked by measuring S and ρ for pure liquid Ni and comparing the values obtained with those reported by Howe and Enderby (1973). A satisfactory degree of agreement was achieved. The results for the liquid alloy system are presented in figures 1 and 2.

3. Discussion

The direct comparison of equation (1) with experimental observations on pure liquid transition metals is extremely difficult; this is because the value of A is somewhat arbitrary (depending as it does on the choice for E_F and k_F) and because $\sin^2 \eta_2(\epsilon_F)$ depending as it does on the choice for E_F and k_F and because $\sin^2 \eta_2(\epsilon_F)$ depends sensitively on the position and the width of the d-resonance. Furthermore, in the low-momentum transfer region, the absolute value of $a(2k_F)$ is uncertain to perhaps as much as 50%.

One way round this difficulty is to replace $a(q)|t|^2$ in the expression for ρ and S by

$$\langle T_{\text{alloy}} \rangle^2 = c_1 |t_1|^2 (1 - c_1 + c_1 a_{11}(q)) + c_2 |t_2|^2 (1 - c_2 + c_2 a_{22}(q)) + c_1 c_2 (t_1^* t_2 + t_1 t_2^*) (a_{12}(q) - 1)$$

where c_1 and c_2 are the concentration of the two types of ion and an obvious notation is used to label the transition matrices and the structure factors; we then assume that the parameters needed to evaluate T for the liquid alloy can be derived directly from the properties of the pure components. It then follows by straightforward extensions of equations (1) and (2) to the alloy case that the resistivity and the thermoelectric power of the alloy are given by

$$\rho_{\text{alloy}} = \alpha c^2 + \beta c + \gamma \tag{3}$$

$$S_{\text{alloy}} = \alpha' c^2 + \beta' c + \gamma' \tag{4}$$

where c is the atomic fraction of component 1. The full expression for $\alpha, \beta \dots \gamma'$ will not be reproduced here. Apart from ϵ_F and k_F , which we treat as coupled parameters, $\alpha, \beta \dots \gamma'$ are defined completely by the thermoelectric power and resistivity of the pure

components 1 and 2. It therefore remains to decide a value of \bar{a} , $\partial\bar{a}/\partial\epsilon$ and ϵ_F ; the following schemes were tried.

Scheme 1

The effective valency (Z) was chosen as unity and k_F fixed at a value of 1.33 \AA^{-1} . To allow for uncertainties in the muffin-tin zero, ϵ_F was allowed to depart from the free-electron value by ± 0.02 Ryd. The structure factor used was the average of those appropriate to pure liquid Ni and pure liquid Co (Waseda and Ohtani 1975) and the error on \bar{a} was assumed to be ± 0.02 subject to the condition that \bar{a} must not be less than the long-wavelength limit. The error on $(\partial a/\partial q)|_{\epsilon_F}$ was taken as $\pm 10\%$. The results are shown in figure 3(a); the range of calculated values found when the input parameters are allowed to vary in the manner specified above fall within the thickness of the theoretical line. Thus the predicted variations of S and ρ with concentration, $S(c)$ and $\rho(c)$, do not agree with experiment.

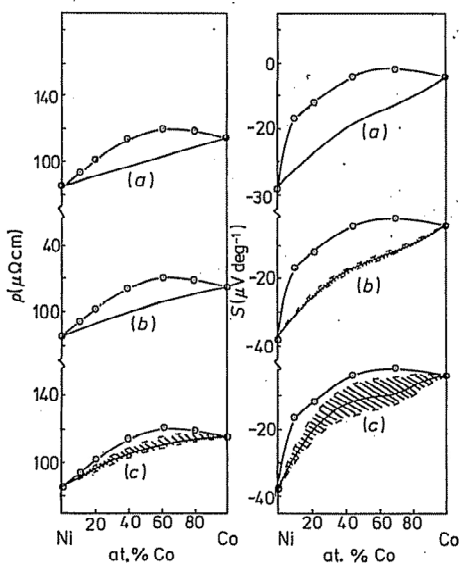


Figure 3. Resistivity and thermoelectric power of liquid Co-Ni alloys. Circles give experimental results; shaded areas give theory according to scheme 1(a), scheme 2(b) and scheme 3(c).

Scheme 2

Scheme 1 was followed except that Z was chosen as 0.46 (Brown 1973) so that k_F becomes 1.02 \AA^{-1} and \bar{a} is changed accordingly. Once again the calculated values of the transport coefficients (figure 3b) are not very sensitive to errors in the input parameters.

Scheme 3

Scheme 1 was again followed but this time Z was taken as 0.2. In this case (figure 3c) the calculated properties are very sensitive to the input parameters. It does appear, however, that if such a low value of Z is used, the theory can account qualitatively for

the general form of $S(c)$ and $\rho(c)$, particularly when allowance is made for the rather crude approximations made in deriving equations (3) and (4).

4. Conclusions

The analysis we offer of our experimental data suggests that the single-site resonance method can be applied to liquid Ni-Co if low values of Z can be assumed. On the other hand, for Z values usually quoted in the literature, the predicted forms of $\rho(c)$ and $S(c)$ are essentially independent of the choice of ϵ_F , \bar{a} and $(\partial a/\partial q)|_{\epsilon_F}$ and do not agree with experiment. Further work is clearly necessary if the general validity of small effective valences is to be established with confidence.

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