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Excess molar volume and m/m^* effects in the magnetic behaviour of liquid HgNa alloys†

A Extremera

Departamento de Física Moderna, Facultad de Ciencias, Universidad de Granada,
E-18071 Granada, Spain

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Abstract. The magnetic susceptibility of liquid-mercury-based alloys containing 5, 8, 15 and 18 at. % Na is investigated. Changes in the paramagnetic contribution of the conduction electrons are discussed in terms of negative excess molar volume. The anomalous variation of the total magnetic susceptibility with the composition is analysed. The occurrence of Hg₄ units appears to be corroborated from the composition dependence of the effective mass ratio m/m^* .

1. Introduction

In an earlier work (Extremera 1988) two interesting features of magnetic properties were observed in liquid-Hg-based alloys containing sodium: one is the very large reduction in diamagnetism produced when an exceedingly small quantity of sodium is introduced into liquid mercury; the other is the tendency towards formation of intermetallic associations with short-range-ordered structures as deduced from the remarkable peculiarities in the concentration dependence curve of the total magnetic susceptibility. The former might require a more detailed study, since one would expect—in principle—a decrease in the paramagnetic component as a result of the negative excess molar volume in the dilute solute concentration range. The latter was speculatively explained by the formation of clusters in which outer-shell electrons could be localized around mercury ions.

For the Hg–Na system, Morikawa *et al* (1987) have recently carried out measurements of the excess molar volume,

$$V_M^{\text{ex}} = V_M - (x_1 V_1^0 + x_2 V_2^0) \quad (1.1)$$

where V_M is the molar volume, x_α is the atomic fraction of component α , and V_α^0 is its molar volume in the pure state. They found that V_M^{ex} has negative values varying linearly with the concentration of Na. Using their measurements obtained by the pycnometer method, we investigate the contribution of V_M^{ex} to the total magnetic susceptibility, it being at first sight tempting to speculate about the part of the susceptibility due to the tightly bound (ion-core) electrons, χ_i . We have extended our analysis up to the concentration 18 at. % Na where the NaHg₄ forms peritectically (Extremera 1982, 1987).

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To determine χ_i , various approximations have been employed in dealing with calculations from self-consistent charge densities (Hurd and Coodin 1967, Feiock and Johnson 1969, Mendelsohn *et al* 1970, Banhart *et al* 1986). However, under the assumption of interacting electrons with an effective mass m^* , calculations of the electronic susceptibility, χ_e , enable us to estimate χ_i if one takes into account the observed values for the total magnetic susceptibility χ_T (Timbie and White 1970). This latter method also leads to the discovery of the composition dependence of the effective mass ratio (or band effective mass in a low-temperature context).

2. Experiment

The procedure for preparing the samples has been described elsewhere (Extremera 1988). The magnetic susceptibilities were determined by means of a modified Gouy method. The temperature was kept nearly constant (18–19 °C) during the measurements. The Gouy tube was made of Pyrex glass with a ground glass stopper and was suspended by a fine copper wire from the centre of the left pan of the balance. Three tubes each 11 cm in length and 0.97, 0.86 and 0.66 cm in diameter, respectively, were used. For each tube, measurements were taken at three different magnetic fields corresponding to current strengths of 5, 6 and 7 A. Hence, using three tubes and three field strengths, nine readings could be taken for a composition.

3. Results and discussion

The total magnetic susceptibility χ_T of simple metals is written as follows

$$\chi_T = \chi_i + \chi_e \quad (3.1)$$

In the free-electron approximation, the contribution of the conduction electrons to χ_T obeys

$$\chi_e = [2\mu_0\mu_B^2 m N_A^{1/3} / \alpha \hbar^2 (3\pi^2)^{3/2}] \bar{z}^{1/3} V_M^{2/3} \quad (3.2)$$

where α is the free-electron mass to effective mass ratio (i.e. m/m^*) and \bar{z} is the average number of valence electrons transferred to the conduction band. N_A , m , μ_B , μ_0 and \hbar have their usual meanings. The expression of χ_e for interacting electrons corrected for effective mass is (Collings 1967)

$$\chi_e = (1 - \frac{1}{3}\alpha^2)\chi_P / [1 - (1 - \alpha)(\chi_P/\chi_P^f)] \quad (3.3)$$

where χ_P^f is the electron spin paramagnetism for free electrons and χ_P is that for 'free' electrons taking into account the Coulomb interaction.

Showing a common tendency of mercury alloys containing alkali metals, V_M^{ex} decreases with increasing solute concentration in the form (Morikawa *et al* 1987)

$$V_M^{\text{ex}} = -9.859 \times 10^{-6} x_{\text{Na}} - 3.76 \times 10^{-7} x^2 \text{ (m}^3 \text{ mol}^{-1}\text{)} \quad (3.4)$$

for the composition range extending to 14.38 at. % Na. From equation (3.2), the fractional change $\delta\chi_e/\chi_e$ of the electronic susceptibility and the volume contraction V_M^{ex}/V_M are related by

$$\delta\chi_e/\chi_e = \frac{2}{3} V_M^{\text{ex}}/V_M \quad (3.5)$$

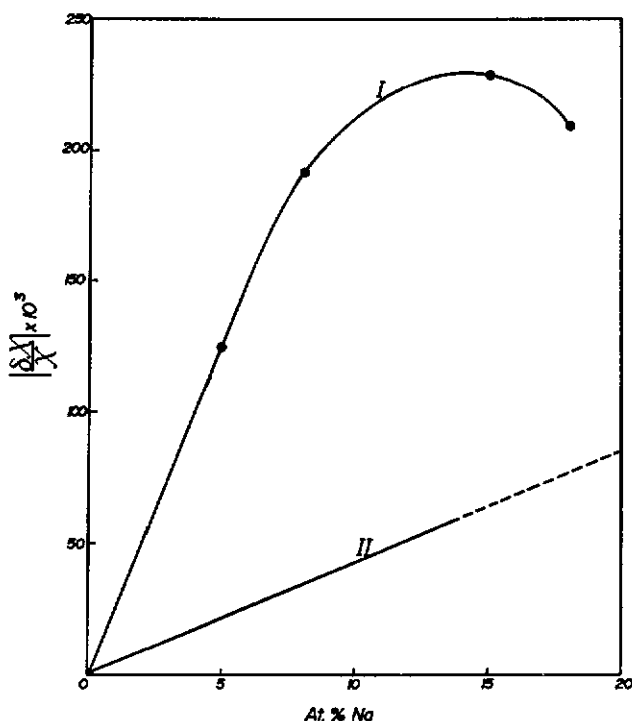


Figure 1. Fractional change of χ_T (curve I) and χ_e (curve II) for various compositions at 18 °C.

assuming $V_M = 15.14 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ as taken from data of Morikawa and co-workers. Since our previous results corroborate characteristic anomalies in the plot of χ_T against composition, we may compare $\delta\chi_e/\chi_e$ with the measured fractional change of χ_T at 18 °C, now focusing our attention on the behaviour of the ion-core contribution. This qualitative analysis might involve the formation of clusters around specific concentrations.

Figure 1 displays the composition dependence of the ratios $|\delta\chi_T/\chi_T|$ (curve I) and $|\delta\chi_e/\chi_e|$ (curve II). The latter, which has been obtained by using equations (3.4) and (3.5), shows a linear variation. It is apparent that the correction of χ_e leads to a small decrease in paramagnetism.

However, the competition between the diamagnetism of the core atoms and the paramagnetism of the conduction electrons appears to be reflected in the curve corresponding to the experimentally observed values of $|\delta\chi_T/\chi_T|$ plotted against at. % Na. When minute quantities of Na are added to the alloy, the Na goes into solution, favouring the paramagnetism as a consequence of the interaction between the Na single spins. When larger quantities of Na are added to Hg, the Na atoms occupy the holes between the zig-zag bands of Hg atoms (Nielsen and Baenziger 1954), forming pairs with diamagnetic behaviour. The prominent diamagnetic deviation around 18 at. % Na suggests the formation of square-planar clusters at the composition NaHg_4 (Corbett 1969).

If we now turn to equation (3.3), Hedin and Lundqvist (1969) have obtained χ_p for metallic mercury using the Fermi liquid theory. The free-electron spin susceptibility, χ_p^f , is estimated from the value of the inter-electronic distance r_s , which is calculated throughout the observed range of densities of metallic mercury (Takahashi and Shimizu 1973). χ_i for pure metals can be estimated by subtracting χ_e calculated with $\alpha = 1$ from

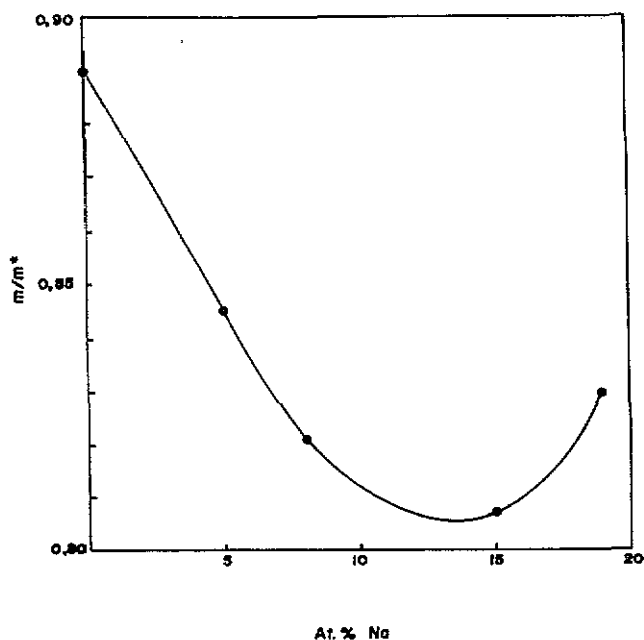


Figure 2. The effective mass ratios in the liquid Hg-Na system up to 20 at. % Na.

the experimental values χ_T . If χ_i^{Hg} and χ_i^{Na} remain unchanged on alloying, we can determine the composition dependence of m/m^* using χ_T for each composition. The result for the liquid Hg-Na system containing less than 20 at. % Na is shown in figure 2. The initial fall in m/m^* corroborates the increase of the paramagnetic enhancement ($m^* > m$) in the case of very dilute alloys. Thus, the structure of the liquid Hg-Na system is not far from that of a random mixture of atoms. Nevertheless, in the range of concentrations where the Hg_4 units are clearly bridged by the Na atoms the paramagnetic enhancement would be drastically reduced because of a redistribution of the electrons (Shimoji *et al* 1988).

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