



**HAL**  
open science

# ELECTRICAL RESISTIVITIES OF RARE EARTH SOLUTES IN LIQUID INDIUM AND TIN

S. Ohno, F. Kakinuma

► **To cite this version:**

S. Ohno, F. Kakinuma. ELECTRICAL RESISTIVITIES OF RARE EARTH SOLUTES IN LIQUID INDIUM AND TIN. *Journal de Physique Colloques*, 1980, 41 (C8), pp.C8-527-C8-530. 10.1051/jphyscol:19808133 . jpa-00220231

**HAL Id: jpa-00220231**

**<https://hal.science/jpa-00220231v1>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## ELECTRICAL RESISTIVITIES OF RARE EARTH SOLUTES IN LIQUID INDIUM AND TIN

S. Ohno and F. Kakinuma

*Niigata College of Pharmacy, 5829, Kamischin-eicho, Niigata, Japan*

Abstract. - The residual resistivities of rare earth solutes in liquid In and Sn increase gradually from La to Nd, peak at Nd and decrease gradually from Nd to Yb. Since the conduction electrons of simple liquid metals may be treated as nearly free electrons, the residual resistivity consists of two terms; the first due to the impurity potential and the second due to the spin scattering. The spin scattering term has a maximum at Gd. The trend of residual resistivities in liquid In and Sn does not agree with the calculated values of spin scattering. Therefore, it seems that the impurity potential is a major term and the spin scattering is a minor term in liquid In and Sn.

## § 1. Introduction

Recently several experimental works have been carried out to understand the behaviour of the 4f and 5d electrons in the liquid metals.<sup>1,2)</sup> The 4f electrons of rare earth (RE) metals lie deep inside the  $5s^2 5p^6$  closed shell, so that the effective number of Bohr magneton has been successfully explained by the Hund's rules.

The electrical resistivities of RE metals have a maximum for Gd at low temperatures. Similarly, the residual resistivities of dilute RE alloys as a function of RE elements are mainly explained by the effect of magnetic scattering due to the s-f exchange interaction.<sup>3)</sup>

However, the electrical resistivities of liquid RE metals increase monotonically across the RE series from La to Er.<sup>1)</sup> The electronic behaviour of pure RE metals shows a considerably large difference in the solid and liquid states. The additional resistivities of RE solutes in liquid Sn have been mainly explained by the effect due to the s-d or s-f resonance scattering and the distortion effect due to the lanthanide contraction.<sup>4)</sup> The mag-

netic scattering is a minor term in the case of liquid Sn with RE solutes. From the experimental results of electronic properties, we will discuss the influence of the 4f and 5d electrons in liquid In and Sn.

## § 2. Experimental Procedure

The magnetic susceptibility apparatus used in this experiment is the Faraday method due to a torsion balance. Details of the apparatus have been described in a previous paper.<sup>4)</sup> As the standard sample we used Mohr's salts ( $\chi = 1.26 \times 10^{-2}$  cgsemu/mol at room temperature). Measurements of the susceptibilities were carried out under the condition of  $H = 12000$  Gauss and  $H \cdot dH/dx = 12.6 \pm 0.5$  (k-Gauss)<sup>2</sup>/cm. The alloys sample of about 3 g was put into the vacuum sealed quartz tube. This sample was kept at high temperatures for several hours before measurements.

The electrical resistivity apparatus used in this experiment is essentially the same as before.<sup>4)</sup> The liquid specimen is in the alumina crucible which is held by stainless steel rod. When the specimen is heated up to a required temperature, the

stainless steel rod is moved to a resistivity cell which has a small hole at the bottom in order to push the liquid specimen into the cell. This rod was often repeated to move up and down during the measurements for degassing. Measurements were carried out at pressures about  $10^{-5}$  Torr. A digital voltmeter with the accuracy of  $10^{-8}$  volt was used for measurements. The purity of In and Sn is 99.99 at % and that of RE metals is 99.9 at %.

§ 3. Experimental Results

The additional susceptibility of La solute is small positive value for liquid In and Sn. This value is explained by the concept of virtual bound state.

The additional susceptibility of Ce, Pr and Nd solutes is experimentally written by

$$\Delta\chi = N\{g_J^2\mu_B^2 J(J+1)/3kT + \alpha\} \quad (1)$$

where N is the number of magnetic ion per unit volume, J is total angular moment,  $g_J$  is Lande's factor,  $\mu_B$  is Bohr magneton and  $\alpha$  is a temperature independent term which will be discussed later.

The effective magneton number P and constant parameter  $\alpha$  were determined by eq. (1) as given in Table 1.

Table 1.

The effective Bohr magneton numbers (P) and Van Vleck terms ( $\alpha$ ) of Ce, Pr and Nd solutes in liquid In and Sn.

$$(\alpha \times 10^{+6} \text{cgsemu.}, P = g_J\sqrt{J(J+1)})$$

		Ce	Pr	Nd
In	$\alpha$	1.56	5.19	8.90
	P	1.78	3.14	3.17
Sn	$\alpha$	7.42	11.9	14.6
	P	1.49	2.50	2.57

The additional susceptibilities of Gd, Dy and Er in liquid In and Sn agree with Curie law ( $\alpha = 0$ ). The effective magneton numbers agree with the calculated values of trivalent RE ion using Hund's rules.

The temperature dependences of electrical resistivities of liquid In and Sn with RE solutes have been measured from the melting point to about 1000 °C. Mattiessen's rule is satisfied for dilute RE alloys. These experimental results give a linear relationship between the residual resistivity and concentration of RE solute. These values of residual resistivities are given in Table 2.

§ 4. Discussion

The additional susceptibilities of liquid In and Sn with Gd, Dy and Er solutes obey the Curie law. This means that the 4f electrons of heavy RE ions lie deep in-

Table 2.

The additional resistivities of RE solutes  $\Delta R$  (1 at %) and the number of 5d electrons  $n_d$  per RE ion in liquid In and Sn.

		La	Ce	Pr	Nd	Sm	Gd	Dy	Er	Yb
In	$\Delta R$ ( $\mu\Omega$ -cm)	1.58	2.13	2.50	2.64	1.94	2.07	1.23	1.51	1.45
	$n_d$	1.75	2.08	2.29	2.37	1.97	2.05	1.53	1.71	1.67
Sn	$\Delta R$ ( $\mu\Omega$ -cm)	3.13	—	3.63	3.85	1.74	1.22	1.03	1.91	1.85
	$n_d$	3.45	—	4.02	4.38	2.29	1.86	1.69	2.43	2.38

side the  $5s^2 5p^6$  closed shell and satisfy the condition  $(E_J - E_{J'}) \gg kT$  where  $E_J$  is the energy level of multiplet. The 4f electrons of heavy RE solutes locate completely far from the conduction electrons.

In the case of light RE solutes, the experimental magneton numbers in liquid In and Sn are smaller than the calculated values of trivalent RE ion using Hund's rules. The constant parameters  $\alpha$  in liquid In and Sn are considerably larger than the calculated values determined by applying Van Vleck Theory.<sup>5)</sup> It seems that the constant parameter  $\alpha$  of each RE solute increases with increasing the values of  $k_F$  of host metals. In order to explain these facts, we assume that the increasing of  $\alpha$  might be related to the enhancement of s-f mixing which is caused by the increasing Fermi energy of host metals. De Wijn *et al.*<sup>6)</sup> have shown that in general the effective exchange integral varies with the Fermi wave number  $k_F$ .

The additional susceptibility of Sm solute is explained by taking into account the excited states. Its temperature dependence is calculated from the multiplet of the excited level.

The electrical resistivity of dilute RE alloys is written by

$$R = R_0 + R_a + R_m \quad (2)$$

where  $R_0$  is the lattice resistivity of the host metal,  $R_a$  is the resistivity due to the impurity potential and  $R_m$  is that due to spin scattering. The expression of  $R_m$  has been given by de Gennes as<sup>7)</sup>

$$R_m = \frac{\pi m D(E_F)}{n e^2 \hbar} c (g_J - 1)^2 J(J+1) J_{ex}^2 \quad (3)$$

where  $D(E_F)$  is the density of states at the

Fermi level,  $n$  is the electron number per unit volume and  $J_{ex}$  is the effective exchange energy. The electrical resistivity of pure RE metals is explained from this term at low temperatures. The curve of residual resistivity of dilute RE alloys vs RE elements has a maximum at Gd solute<sup>3)</sup> and does not agree with those of RE solutes in liquid In and Sn. Therefore, it seems that the impurity scattering is a major term and the magnetic scattering is a minor term in the case of liquid In and Sn with RE solutes.

The impurity potential involves some effects due to the resonance scattering, the redistribution of the conduction electrons around the impurity atom and the lattice distortion around it. The unfilled f-shell exerts two influence of resonance scattering and lattice distortion upon the residual resistivity. Roughly speaking, the residual resistivities change smoothly from La to Yb. Since the radii of RE ions change smoothly from La to Yb, the residual resistivity due to the lattice distortion might be resulted from the lanthanide contraction of unfilled f-shell.

On the other hand, Duthie and Pettifor showed the curves of  $N_{5d}$  as a function of volume for both La and Lu.<sup>8)</sup> From the results at equilibrium, La has approximately 0.6 d electrons more than Lu. Güntherodt *et al.*<sup>1,9)</sup> indicate that the electrical resistivity of RE metals is due to the resonance scattering by the 5d and not the 4f states. According to the analysis of phase shift, the number of d electrons per RE solute atom changes from 2.5 for La to 1.5 for Lu. These results are concerned

with the lanthanide contraction of RE ions. Therefore, we discuss the effective number of  $N_{5d}$  on the basis of the results of residual resistivity.

We assume that the phase shift  $\eta_0$  and  $\eta_1$  are little change in such a dilute alloy as concerning with that of host metal and that only  $\eta_2$  should be an additional term to the resistivity. The residual resistivity of 5d resonance is given by

$$R_a = \frac{20 \pi \hbar c}{n_A e^2 k_F} \sin^2 \eta_2(E_F) \quad (4)$$

where  $n_A$  is the number of conduction electrons per solvent atom. Using Friedel sum rule, the phase shift  $\eta_2$  is given by

$$\eta_2 = \frac{\pi}{10} N_{5d} \quad (5)$$

where  $N_{5d}$  is the number of localized 5d electrons. According to the experimental

results, the effective number of  $N_{5d}$  is calculated from eqs.(4) and (5) as given in Table 2. These values increase gradually from La to Nd, peak at Nd and decrease gradually from Nd to Yb.

In the case of RE solutes, the large values of  $N_{5d}$  might be related to the s-f mixing between 4f and conduction electrons. Therefore, the additional susceptibility deviates from the Curie law. The 4f electrons of light RE solutes interact considerably with free electrons, so that the residual resistivity gives rise to a large values.

On the other hand, the 4f electrons of heavy RE solutes are located inside  $5s^2 5p^6$  shell. Therefore, this effect gives rise to a small value of residual resistivity and the additional susceptibility agrees with the Curie law.

#### References

- (1) Delley, B., Beck, H., Künzi, H. U. and Güntherodt, H. -J., *Phys. Rev. Lett.* 40 (1978) 193.
- (2) Rigert, J. A. and Flynn, C. P., *Phys. Rev.* B5 (1972) 4569.
- (3) Sugawara, T. and Eguchi, H., *J. Phys. Soc. Jpn.* 21 (1966) 725.
- (4) Ohno, S., *J. Phys. Soc. Jpn.* 44 (1978) 819.
- (5) Araj, S. and Colvin, R. V., *Rare Earth Research* (The Macmillan Company, New York) 1961.
- (6) DE Wijn, H. W., Buschow, K. H. J. and Van Diepen, A. M., *Phys. Stat. Sol.* 30 (1968) 759.
- (7) DE Gennes, R. G., *J. Phys. Rad.* 23 (1962) 510.
- (8) Duthie, J. C. and Pettifor, D. G., *Phys. Rev. Lett.* 38 (1977) 564.
- (9) Güntherodt, H.-J. and Zimmermann, A., *Phys. Kondens. Materie* 16 (1973) 327.