ELECTRONIC CONTRIBUTION TO THE ENTROPY OF MIXING OF LIQUID TRANSITION METAL BASED ALLOYS
S. Khanna, F. Cyrot-Lackmann, P. Hicter

To cite this version:
S. Khanna, F. Cyrot-Lackmann, P. Hicter. ELECTRONIC CONTRIBUTION TO THE ENTROPY OF MIXING OF LIQUID TRANSITION METAL BASED ALLOYS. Journal de Physique Colloques, 1980, 41 (C8), pp.C8-582-C8-585. <10.1051/jphyscol:19808147>. <jpa-00220246>

HAL Id: jpa-00220246
https://hal.archives-ouvertes.fr/jpa-00220246
Submitted on 1 Jan 1980

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.
ELECTRONIC CONTRIBUTION TO THE ENTROPY OF MIXING OF LIQUID TRANSITION METAL BASED ALLOYS

S.N. Khanna, F. Cyrot-Lackmann and P. Hicter

*Groupe des Transitions de Phases, C.N.R.S., B.P. 166, 38042 Grenoble Cedex, France.

Abstract.- Experimental results on the entropy of mixing of liquid transition metal based alloys FeSi, CoSi and NiSi show that there is an exceptionally negative entropy of mixing. We have shown that this effect is due to the electronic contribution of entropy which is proportional to the density of states at the Fermi level. As the transition metal is alloyed with Si, the free valence electrons of Si produce an s-d transfer leading to a filling of the d-band of the transition metal. This leads to a decrease of entropy when alloying due to decrease in density of states at the Fermi level. Our numerical results show good agreement with experiments. We have also been able to ascribe the change in the concentration of Si, for minimum entropy, as due to the difference in the filling and the shape of the d-bands in the pure liquid Fe, Co and Ni metals.

INTRODUCTION

Experimental measurements on the entropy of mixing (1,2), \( \Delta S_M \), in liquid alloys A Si, where A is a transition metal Fe, Co or Ni, show that there is an exceptionally negative minima in \( \Delta S_M \) at a certain Si concentration. Also, the Si concentration corresponding to the minima decreases as one moves, from Fe to Co to Ni.

Very recently, Khanna et al (3) have proposed a model to explain the above results. The basic idea of the model is that as a pure transition metal, with its high electronic entropy, due to high d-density of states, is alloyed with Si, there is a change in the electronic entropy due to the filling of the d-band because of the charge transfer. The increasing Si concentration leads to a decrease of the d-electronic contribution until at a certain critical concentration \( \chi_{Si} \), the d-band is filled and the d-electronic contribution becomes zero. Beyond \( \chi_{Si} \), there is a slight change in electronic entropy, due to increasing number of s-electrons, as the Si concentration is increased. In the actual application, it was supposed that in the concentration region \( 0 < \chi_{Si} \leq \chi \), the d-density of states of the transition metal decreases linearly with \( \chi_{Si} \). It is easy to show that this first approximation implies an exponential tail of the density of d-states. Such an approximation is good in the vicinity of \( \chi_{Si} \), but is not so good in the low Si concentrations.

The aim of the present paper is to present and compare results by taking another approximation for the change in the density of d-states, namely, the rigid band model, within the same philosophy. Contrary to our earlier calculations, the rigid band model is likely to be a better model in the low Si concentrations but is likely to become approximate in the vicinity of \( \chi_{Si} \).

In Section I, we shall briefly review the model and develop the rigid band approximation. Section II is devoted to the details of calculations and discussion of results.

I. CALCULATION OF ELECTRONIC AND MAGNETIC ENTROPY

The entropy of mixing \( \Delta S_M \) is given by the expression ;

\[
\Delta S_M = \Delta S_{id} + \Delta S_{el}^{xs} + \Delta S_{mag} + \Delta S_{conf}^{xs} + \Delta S_{vib}^{xs} \tag{1}
\]

Here \( \Delta S_{id} \) is the ideal contribution, \( \Delta S_{el}^{xs} \) is the
The magnetic contribution from the transition metal ion, $\Delta S_{\text{mag}}$, is defined as:

$$
\Delta S_{\text{mag}} = S_{\text{el}} - x_A S_A^{\text{conf}} - x_{\text{Si}} S_{\text{Si}}^{\text{conf}}
$$

(3)

The configurational contribution, $\Delta S_{\text{conf}}$, is given by the expression:

$$
\Delta S_{\text{conf}} = -R \left[ x_{\text{Si}} \ln \left( 1+x_{\text{Si}} \right) + x_A \ln \left( 1+x_A \right) \right]
$$

(2)

The vibrational contribution, $\Delta S_{\text{vib}}$, is the ideal vibration contribution from the transition metal ion, $A$, and is given by the expression:

$$
\Delta S_{\text{vib}} = -R \left[ x_{\text{Si}} S_A^{\text{vib}} + x_A S_A^{\text{vib}} \right]
$$

(1)

where $x_A$ is the concentration of the transition metal ion and $R$ is the gas constant.

The sum $\Delta S_{\text{conf}} + \Delta S_{\text{vib}}$ is likely to be small in these systems and can be neglected. So the calculation of $\Delta S_{\text{M}}$ requires knowledge of $\Delta S_{\text{conf}}$, $\Delta S_{\text{vib}}$, and $\Delta S_{\text{mag}}$. These can be expressed as:

$$
\Delta S_{\text{el}}^{\text{mag}} = S_{\text{mag}} - x_A S_A^{\text{mag}} - x_{\text{Si}} S_{\text{Si}}^{\text{mag}}
$$

(3a)

Here, $S_{\text{el}}$ and $S_{\text{mag}}$ are the entropies of the alloy systems and $S_A^{\text{mag}}$ and $S_{\text{Si}}^{\text{mag}}$ are the corresponding entropies in the pure systems.

1. $0 \leq x_{\text{Si}} \leq \frac{x}{x_{\text{Si}}}$

In this concentration region, there is a filling of the d-band of the transition metal and for the sake of mathematical simplicity it was firstly assumed (3) that the d-density of states $n_{\text{DF}}$ for a concentration $x_{\text{Si}}$ shows a linear decrease:

$$
n_{\text{DF}} = n_{\text{DF}}^0 - x_{\text{Si}} \frac{n_{\text{DF}}^0}{x_{\text{Si}}^0} (1-\frac{x_{\text{Si}}}{x_{\text{Si}}^0})
$$

(4)

Using the relation between entropy and the density of states (3), the d-contribution to the entropy is given by:

$$
S_{\text{el,d}} = \frac{1}{3} \ln \frac{2}{\pi} T n_{\text{DF}}^0 A \left( \frac{x_{\text{Si}}}{x_{\text{Si}}^0} \right)
$$

(5)

Further it was assumed (3) that in the present concentration range each Si loses $n_{\text{Si}}^{\text{Si}A}$ out of its four electrons to the d-band of the transition metal. The average number of free electrons per atom is then given by:

$$
\bar{\pi} = x_A S_A^0 + x_{\text{Si}} (4-n_{\text{Si}}^{\text{Si}A})
$$

(6)

where $\bar{\pi}$ is the number of s-electrons per transition metal. Taking a free electron model for the density of states and taking the atomic volume $V = x_A V_A + x_{\text{Si}} V_{\text{Si}}$ with $V_A$ and $V_{\text{Si}}$ as atomic volumes in pure A and Si respectively, the sp contribution to the entropy is given by (3):

$$
S_{\text{el,sp}} = \frac{1}{3} \left[ \frac{2}{3} x_A S_A^0 + x_{\text{Si}} (4-n_{\text{Si}}^{\text{Si}A}) \right]^{1/3} \left[ \frac{1}{2} x_{\text{Si}} S_{\text{Si}}^{\text{sp}} + \frac{2}{3} x_A S_A^{\text{sp}} \right]^{1/3}
$$

(7)

Combining (5) and (7) one gets:

$$
\Delta S_{\text{el}}^{\text{mag}} = -x_A S_A^{\text{mag}} - x_{\text{Si}} S_{\text{Si}}^{\text{mag}}
$$

(8)

Taking again, a linear variation for the magnetic term, one gets:

$$
\Delta S_{\text{mag}} = x_{\text{Si}} S_{\text{Si}}^{\text{mag}}
$$

(9)

In this range, the d-band of the transition metal is full. The number of s-electrons per atom is given by the expression:

$$
\bar{\pi} = 4 x_{\text{Si}} + x_A S_A^0 - x_A n_A
$$

(10)

where $n_A$ is the number of holes in the d-band of A.

As before, the entropies given by (3) and (10) can be expressed as:

$$
\Delta S_{\text{el}}^{\text{mag}} = -x_A S_A^{\text{mag}} - x_{\text{Si}} S_{\text{Si}}^{\text{mag}}
$$

(11)

and:

$$
\Delta S_{\text{mag}} = \left[ x_{\text{Si}} S_{\text{Si}}^{\text{mag}} \right]
$$

(12)

The two assumptions, namely, a linear decrease of the density of states with $x_{\text{Si}}$ (Eq. 4), and that each Si atom loses $n_{\text{Si}}^{\text{Si}A}$ electrons to the d-band imply an energy dependence, for the d-band density of states, of the form:

$$
\bar{\pi} = n_{\text{DF}}^0 \left[ x_{\text{Si}} S_{\text{Si}}^{\text{mags}} \right] / (E_F - E_A)
$$

(13)

where $E_F^A$ is the Fermi energy in pure A.

Two of the present authors have studied density of d-states in amorphous or liquid transition metals (4, 6). In Fig. 1, we have schematically shown the density of d-states and the position of Fermi level in the liquid transition metals. As seen from this figure, the density of d-states varies almost linearly with the energy $E$. If we take a rigid band picture, i.e. assume that the d-band is not defor-
Fig. 1: Density of d-states using model obtained by relaxing a dense H.S. model under Lennard-Jones potential.

Fig. 2: Integral entropy of mixing \( \Delta S_M \) in Fe-Si:
- Calculated values using H.S. (---) and relaxed model (----) density of states:
- Experimental values: -.-.- first approximation values.

\[ n_{Si}^* = \frac{n_A}{n_{Si}^* + n_{Si-A}} \]

that the minima in experimental \( \Delta S_M \) is close to \( x_{Si}^* \). Using \( n_A \) values \(^{(7–9)}\) of 3, 1.6 and 0.6 along with \( x_{Si}^* \) values \(^{(1,2)}\) of 0.6, 0.5 and 0.35, we obtain \( n_{Si-A} \) values of 2, 1.6 and 1.1 for Fe, Co and Ni respectively.

\( \Delta S_M \) results are obtained by using d-electronic entropies \( S_{A,d}^0 \) of Fe, Co and Ni based on density of states from hard-sphere \(^{(5)}\) and Lennard-Jones \(^{(6)}\) relaxed models respectively. These values are 3.8, 4.2 and 4.2 cal mole\(^{-1}\) K\(^{-1}\) for the hard-sphere model and 3.6, 3.6 and 3.3 cal mole\(^{-1}\) K\(^{-1}\) for the Lennard-Jones model, for Fe, Co and Ni respectively.

For the magnetic entropies \( S_{Mag}^0 \) of Fe, Co and Ni we have used the values of 1.4, 1.6 and 0.93 cal mole\(^{-1}\) K\(^{-1}\) of Lytton \(^{(10)}\). Our calculated \( \Delta S_M \) values for Fe, Co and Ni are shown in Figs. 2-4 respectively, along with the experimental values, and the values based on the first approximation \(^{(3)}\) (only results based on the relaxed model are presented for this case).
Fig. 3: Integral entropy of mixing $\Delta S_M$ in Co-Si: 
Calculated values using H.S. (---) and relaxed model (---) density of states; O experimental values; ---- first approximation values.

From Figs. 2-4, it is seen that the theoretical curves are in qualitative agreement with experiment. A comparison of the results based on the two approxima-