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INFLUENCE OF THE LOCAL CHEMICAL ORDER ON THE ELECTRONIC PROPERTIES IN TRANSITION METAL-POLYVALENT METAL ALLOYS

D. Nguyen Manh, D. Mayou, A. Pasturel, F. Cyrot-Lackmann

Laboratoire d'Etudes des Propriétés Electroniques des Solides, C.N.R.S.,
B.P. 166, 38042 Grenoble Cedex, France

Laboratoire de Thermodynamique et Physicochimie Métallurgiques, E.N.S.E.E.G.,
B.P. 44, 38401 St Martin d'Hères, France

Résumé :

Les effets d'hybridation sur la structure électronique des alliages métaux de transition - métaux polyvalents sont étudiés à partir de la Cluster Bethe Lattice Méthode. Nous montrons que la densité d'états de ces alliages est caractérisée par la présence d'un pseudogap au sommet de la bande d. Leurs propriétés physiques sont discutées en relation avec l'existence de ce pseudogap.

Abstract :

The Cluster Bethe Lattice Method is used for a quantitative study of hybridization effects in transition metal-polyvalent metal alloys. It is shown that the electronic density of states around equiatomic composition is characterized by the occurrence of a pseudo-gap near the top of the d band. Implication of this pseudogap for anomalous physical properties are discussed.

1 - INTRODUCTION

The theoretical studies and experimental measurements of the electronic structure and properties of non-crystalline metallic alloys have aroused a great deal of interest in recent years. Of particular interest were transition metal-polyvalent metal (TP) alloys in which :

i) The hybridization effects were observed in photoemission spectra /1/.

ii) The chemical short range order was observed by diffraction means /2/.

As the local structure seems to be of great importance, the purpose of the present work is to study its influence on the density of states of these alloys.

2 - MODEL ALLOY

To investigate the electronic structure of these alloys, we use the Cluster Bethe Lattice Method including charge transfer effects /3/. The alloy C.B.L.M. is an approximate technique for calculating the averaged local density of states of an alloy replacing the real lattice by a Bethe lattice with the same coordination number and geometrical atomic environment. In such a formalism, the mean local environment of an atom is reproduced very well while the remainder of the alloy is replaced by an effective field, in this case a self-energy /4/. The environment of an atom is then characterized by the geometrical arrangement of the neighbouring sites but also the repartition of the species on these sites. In order to study the first contribution, we present results for a simple single atom cluster with two specific local environments : one which simulates a disordered compact structure (i.e. the mean local environment is isotropic) and the other with local structure of B.C.C. type /5,6/. From fig. 1, we can see that the calculated densities of states have roughly the same shape in both cases but with less structure in the disordered one. For this type of alloy we can conclude that the geometrical local environment does not play a major role in the electronic structure, as it has been already pointed out /7/..
Fig. 1 - Densities of states calculated for Co$_{50}$Al$_{50}$ according the geometrical environment; solid line: BCC symmetry; dots: isotropic symmetry.

Fig. 2 - Densities of states calculated for Co$_{50}$Al$_{50}$; solid line: $\sigma = -0.95$ dashed line: $\sigma = 0$. 
To study the second contribution, i.e. the chemical local environment, we introduce the pair probabilities which are the simplest macroscopic to measure the degree of short range order, S.R.O., in an alloy. These pair probabilities can be related to the S.R.O. parameter $\sigma$ in the following way:

$$p_{ij} = x_i + (1-x_i) \sigma \quad \text{and} \quad p_{ij} = (1-x_i) (1-\sigma)$$

In real systems, $\sigma$ is a priori unknown and its value must be determined from minimization of the free energy /6/. The free energy minimum occurs at $\sigma$ values, $\sigma_{MIN}$, which are very close to the maximum order value. This behaviour is general for all studies alloys and fig. 2 displays densities of states of Co$_{50}$Al$_{50}$ alloy calculated with $\sigma = 0$ and $\sigma_{MIN} = -0.95$. We can see that the evolution of the D.O.S. is very important, S.R.O. being responsible for the creation of structures in the D.O.S. The density of states calculated with $\sigma_{MIN}$ is very similar to the one obtained from band structure calculations for corresponding compounds /8/. More particularly we find that the D.O.S. is characterized by the occurrence of a pseudogap at the top of the d band in the both cases. For Co$_{50}$Al$_{50}$ alloy, fig. 2 shows that the Fermi level is located in the pseudogap that allows us to explain the peculiar behaviour of this alloy around the equiatomic composition. We wish to point out that this critical composition can be estimated from a simple sum rule involving the formation of bonding and antibonding states located on the both sides of the pseudogap /9/. For Fe$_{50}$Al$_{50}$ alloy, the Fermi level lies on the left hand side of the pseudogap while the Fermi level of Ni$_{50}$Al$_{50}$ alloy is on the right hand side. These relative positions of the Fermi level reflect the approximate validity of rigid band theory, i.e. a different filling of an unchanging density of states according to the alloy valence /10/. Table 1 shows the behaviour of the partial densities of states at the Fermi level as a function of composition for the d band of the transition metal and s,p bands of the polyvalent metal. The orbitals at $E_F$ have not the same character in each of these alloys.

**TABLE 1**

Partial densities of states at the Fermi level for (Ni, Co, Fe)$_{x}$-Al$_{1-x}$

<table>
<thead>
<tr>
<th>MT$<em>x$Al$</em>{1-x}$</th>
<th>$x$ %</th>
<th>Al 3 s</th>
<th>Al 3 p</th>
<th>MT 3 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$<em>x$Al$</em>{1-x}$</td>
<td>45</td>
<td>0.048</td>
<td>0.054</td>
<td>2.891</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.023</td>
<td>0.019</td>
<td>0.419</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.056</td>
<td>0.061</td>
<td>1.151</td>
</tr>
<tr>
<td>Fe$<em>x$Al$</em>{1-x}$</td>
<td>45</td>
<td>0.027</td>
<td>0.019</td>
<td>0.472</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.019</td>
<td>0.007</td>
<td>0.129</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.060</td>
<td>0.044</td>
<td>0.675</td>
</tr>
<tr>
<td>Ni$<em>x$Al$</em>{1-x}$</td>
<td>45</td>
<td>0.182</td>
<td>0.059</td>
<td>0.187</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.081</td>
<td>0.006</td>
<td>0.014</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.078</td>
<td>0.011</td>
<td>0.039</td>
</tr>
</tbody>
</table>

We can see that the Co$_x$Al$_{1-x}$ alloys are characterized by relatively strong d-states density in the composition range $0.45 < x < 0.55$. On the other hand for Ni$_x$Al$_{1-x}$, the SP character predominates while for Fe$_x$Al$_{1-x}$ the d-character is very important. This behaviour confirms the major role played by magnetic properties in
Fe$_x$Al$_{1-x}$ alloys /11/. All these results show that the local environment in disordered alloys is similar to that observed in the corresponding crystalline phase for T.P. alloys.

3 - DISCUSSION OF THE PHYSICAL PROPERTIES OF T.P. ALLOYS

We use the above description to show that the local chemical order is responsible for peculiar properties of these alloys.

T.P. alloys are characterized by exceptionally negative thermodynamic data of mixing and the resulting short range order seems to be the main factor to explain this non-ideal mixing behaviour. The calculated heats of formation for (Fe, Co, Ni)$_x$ - Al$_{1-x}$ are shown in fig. 3. We can see that for equiatomic composition, ΔH minimum is related to the occurrence of the pseudogap and the location of the Fermi level in this pseudogap. The important negative values imply a great stability of these alloys around this composition. In the same manner, we have calculated the electronic contribution to the alloy entropy. As this contribution is related to the D.O.S. at the Fermi level, our results show that the exceptional negative minimum of Δ$S_{el}$ at a certain P composition is also due to the formation of the pseudogap in D.O.S. This behaviour has been phenomenologically explained by Khanna et al. /12/ using a rigid band theory.

![Fig. 3 - Calculated heats of formation as a function of composition for :](image)

The experimental composition dependence of electrical resistivity shows also minimum around equiatomic composition for (Co, Ni)$_x$ - Al$_{1-x}$ /11/. Caskey et al. /11/ explain the behaviour from the simple two bands s-d model proposed by Mott /13/. In this model, the current is carried mainly by the s-electron and the effective relaxation time $\tau_s$ is inversely proportional to the D.O.S. in the d band. Our theoretical analysis /5/ and the D.O.S. calculation confirm this mechanism of conductivity in these alloys. From table 1, it is shown that the conductivity of Co$_x$Al$_{1-x}$ and especially Ni$_x$Al$_{1-x}$ is governed by the s electrons of P metal while
d states dominate for Fe$_x$Al$_{1-x}$. In the first two alloys, the partial D.O.S. at the Fermi level, N$_d$(EF), has a minimum at equiatomic composition which implies also a relation between resistivity minimum and pseudogap.

REFERENCES

13/ Mott N.F., Phil. Mag. 26 (1972) 1249.