DENSITY OF D-STATES IN AMORPHOUS TRANSITION METAL ALLOYS
J. Gaspard

To cite this version:
J. Gaspard. DENSITY OF D-STATES IN AMORPHOUS TRANSITION METAL ALLOYS. Journal de Physique Colloques, 1980, 41 (C8), pp.C8-414-C8-417. <10.1051/jphyscol:19808102>. <jpa-00220197>

HAL Id: jpa-00220197
https://hal.archives-ouvertes.fr/jpa-00220197
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.
DENSITY OF D-STATES IN AMORPHOUS TRANSITION METAL ALLOYS

J.P. Gaspard

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

1. Introduction

Nearly all glassy metals are alloys; the most widely studied in fundamental research are binary (or ternary) alloys of a transition metal (TM) or a noble metal (NM) with a metalloid (P, Si...) or another transition metal. The existence of at least two components facilitates the glass formation even if the origin of the mechanism (difference in atomic size, electronic effect...) is not fully understood. It is interesting to analyze the electronic density of states of amorphous alloys in order to find correlations between the atomic and the electronic structure. It is indeed obvious that there is a relation between the electronic structure responsible of the cohesion and the atomic structure as well as the chemical order.

Considering the limitations in the determination of the atomic structure by standard diffraction techniques (X-ray, neutrons...), the aim of this paper is to investigate which piece of additional information can be got from the electronic spectrum, which is approached experimentally by photoemission spectra (UPS and XPS). 

We performed a series of calculations of the d electronic spectrum of transition metal alloys and we focussed our attention of the effect of short range order both in the bulk and at the surface.

2. Method

The calculation of the electronic spectrum is performed in two successive steps:

a) the creation of an amorphous alloy by quenching a molten alloy and
b) the calculation of the electronic density of states (DOS) of the amorphous alloy. This method, based on simple models for the interactions between atoms in the structure and for the electronic interactions (Hamiltonian) is non selfconsistent regarding the cohesion but it has the advantage to be very flexible. It is able to cover a wide variety of situations including bulk and surfaces of systems with various kinds of disorder. This method has been developed by Gaspard /2/ for degenerate d bands and it has been extensively worked out by Khanna et al. /3/ and Fujiwara /4/. They clearly showed that the average density of states is fairly similar to that of crystalline compact phases (FCC or HCP) for an energy resolution of about .5 eV, corresponding to XPS measurements and compatible with the approximation of the theoretical models. However strong deviations occur in the local densities of states depending on the coordination number and on the local arrangement of the first shell of atoms in a way difficult to analyse.

In this work, we obtained the amorphous alloy structure by a molecular dynamic calculation (see e.g. Verlet /4/) of atoms interaction via Lennard-Jones potentials. The relevant parameters are the density \(\rho\), the atomic sizes \(r_A, r_B\), the temperature...
T, the energy prefactors of the Lennard-Jones potentials \( \epsilon_{AA} \), \( \epsilon_{BB} \), and \( \epsilon_{AB} = \frac{\epsilon_{AA} + \epsilon_{BB}}{2} + \Omega \). \( \Omega \) is the regular solution parameter, the value of which is varied between 0 and 5: a positive value of \( \Omega \) corresponds to a tendency to heteroatomic bond formation. The final configuration is obtained starting from a FCC configuration melted at a temperature \( kT = 2 \) (in \( \epsilon_{AA} \) units; the melting temperature is \( kT = 1.7 \)) and subsequently cooled down.

The electronic density of states is obtained in a tight binding description taking full account of the d degeneracy. The \( \tilde{d}_{dd0}, \tilde{d}_{dd1}, \tilde{d}_{dd6} \) parameters are those given in /5/. Nearest neighbor interaction in the liquid are taken up to the first minimum in the pair correlation function. Only diagonal disorder is taken into account, i.e. depending on the type of atoms, or the atomic level is \( E_A \) or \( E_B \). The density of states is obtained by a continued fraction technique described in /6/.

Twelve coefficients of the fraction are calculated; this corresponds to an energy resolution of \( .3 \) eV.

3. Characterization of the local atomic structure

Various attempts have been made to characterize the local order in amorphous and liquid structures. The Voroni polyhedra statistics /7/ provide a characterization of the local environment and is perhaps in relation with the local electronic properties of mono or divalent metals, but it has no relation with the electronic spectra of transition metals /3/. For the latter, we propose a characterization based on closed circuit statistics, i.e. the number of nearest neighbors (circuits of length 2) and the number of circuits of length 3 \( (\nu_3) \).

Fig. 1 shows the distribution of circuits of length 3 in a pure liquid. As an icosahedral structure corresponds to \( \nu_3 = 30 \) and a FCC or HCP structure to \( \nu_3 = 24 \), one observes that -at least at this level of analysis- the environments similar to that of the compact crystalline phases are in greater number than the (deformed) icosahedral environment.

This shows that the icosahedron is not an important structural unit of the amorphous structure.

4. Density of states of disordered alloys

We performed calculations of the alloy density of states for a series of parameters corresponding to different local environments and different atomic level spacings \( \delta = (E_A - E_B)/W \) (\( W \) = band width). The concentration 20 \% A (80 \% B) is representative of many eutectic concentrations around which amorphous phases forms. The parameters \( \epsilon_{AA} \) and \( \epsilon_{BB} \) are identical.
4.1. Completely disordered alloys

Fig. 2 and 3 show the results for 6 = 0.2 and 6 = 0.4 and Ω = 0. For the largest value of 6, one observes a splitting of the d band in a A-type minority and a B-type majority band as observed experimentally by Oelhafen et al. /8/. Very close results — even in the minority band — are obtained by a single site CPA calculation (dotted line) based on the pure amorphous density of states. This shows the validity of the CPA calculations in the case of complete chemical disorder (Ω = 0), and for a high coordination (Z ≈ 11), as already observed in FCC structures /9/.

4.2. Alloys with short range order

In most of the amorphous alloys, it is generally admitted — and there are partial experimental evidences — that the local order resembles to that of the corresponding crystals. When short range order is present, the single site CPA approximation is by essence no longer valid and numerical calculations have their full interest.

We performed calculations on quenched liquid structures for various values of the regular solution parameter. The larger Ω, the stronger the tendency to form heteroatomic pairs. Figs. 2 and 3 show the quantitative evolution of the spectra when Ω is increased from 0 to 5 (in e units).

The minority band presents variations due to Ω; the bigger Ω, the narrower the bandwidth. However, the magnitude of the variations of the spectrum for realistic Ω values is presumably not large enough to be seen in the photoemission spectrum.

4.3. Surfaces of alloys

It is well established that the surface concentration of an alloy can be very different from the bulk concentration, at the thermodynamic equilibrium. In Fig. 4, we represent the local densities of states at the surface of an alloy without (full line) and with (dotted line) surface segregation effect. We observe an important effect on the local DOS, which can be observed experimentally in the UPS spectrum. In TM alloys, it is possible to estimate the surface concentration at equilibrium from the spectral variations /10/. The surface DOS could also be related to the interesting anticorrosive properties of amorphous alloys, in particular with Cr.
**Fig. 4**: Surface density of states of an alloy.

**REFERENCES**

/1/. H.J. GÜNTHERODT and P. OELHAFEN, this conference (invited review 9).


*The latter shows a characteristic difference between the liquid and amorphous densities of states.*