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ON THE BULK AND SURFACE ELECTRONIC STRUCTURE OF AMORPHOUS TRANSITION METALS

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Abstract.- Amorphous metals are characterized by the absence of a long range periodicity as well as the presence of a local disorder. The study of their electronic properties requires an understanding of the relation between the local disorder and the local electronic structure.

In this work, we have carried out calculations on local density of d-states for bulk and surface of amorphous metals using moments method within tight-binding framework, in conjunction with various existing geometrical models. Our results show that the dominant factor governing the local density of states is the strength and shape of the first peak of the local radial distribution function. In the bulk where this local distribution has only small deviations from the average value, the density of states has a double peaked structure with peaks becoming sharper as the first maxima becomes stronger and peaked. As one goes to the surface, the decrease in the first coordination number leads to a merging tendency towards a single central peak.

These calculations have been used to investigate some physical properties like the resistivity, thermoelectric power and the cohesive energy in amorphous materials.

Over the past few years, there has been a lot of interest in the studies of the electronic structure of topologically disordered systems such as liquid and amorphous metals. These materials are characterized by the absence of long range periodicity as well as the presence of a local disorder. The disordered nature of the atomic structure prevents one from using simplifications introduced by crystal momentum and one is inclined to use electronic structure determination schemes working in the direct space. One of the possible ways which takes good account of the atomic disorder is to use the moments method in conjunction with simulation techniques ⁽¹⁾. Recently, the present authors have used this scheme to study the d-band density of states in amorphous and liquid transition metals ^(2,4). We had presented calculations for the d-band density of states using various simulated models for the amorphous atomic structure in conjunction with tight binding methods involving moments expansion.

The motivation of the present paper is two fold. Firstly, to briefly review our results on the bulk d-density of states in the amorphous transition me-

tals and to extend these studies to the surface electronic structure. Secondly we wish to use our calculated density of states to calculate various physical quantities and to understand the changes in various properties as one goes to the amorphous phase.

The method used for calculating the density of states (D.O.S.) is the moments method and the continued fraction technique within the framework of tight binding approach, well documented elsewhere ⁽⁵⁾. In brief, the method involves a calculation of moments μ_n of the D.O.S. which are related to the trace of the one electron hamiltonian, H , by the relation :

$$\mu_n = \frac{1}{N} \text{Tr } H^n \quad (1)$$

N being the number of atoms. One uses a tight-binding hamiltonian and the set of atomic orbitals to expand the trace. The actual evaluation of the moments then requires the atomic structure for which we use either the simulated geometrical models, or the numerical simulation. In a disordered system one is interested in the average density of states which require configurationally averaged moments

$\langle \mu_n \rangle$. These are calculated by averaging moments on various sites in the cluster.

The passage from the moments to the D.O.S. is effected by the continued fraction technique. The method is particularly useful when the continued fraction coefficients converge rapidly which is the case in amorphous or liquid metals as the D.O.S. is expected to be free from sharp and numerous peaks.

A Study of the D.O.S. is important from two basic motivations. Firstly, the D.O.S. carries the basic electronic structure information and, so, it is important to know the parameters controlling various features of the D.O.S. The theoretical findings can be checked against the available direct experimental information on D.O.S. through XPS, UPS, paramagnetic susceptibility, etc. Secondly, the D.O.S. is an important ingredient for an understanding of the various physical properties like the entropy, cohesive energy, resistivity, thermopower, etc. on which a lot of experimental data is available.

We will, here, mainly discuss the various factors governing the D.O.S. We emphasize that the shape of the D.O.S. in amorphous metals is independent of the structural model or the form of the interatomic potential. Indeed, in a recent paper ⁽⁴⁾, the present authors had presented results on the density of d-states in amorphous Co using H.S. models ⁽⁶⁾ and models obtained by relaxing ⁽⁶⁾ a dense H.S. model under Lennard Jones (L.J.), Morse and Truncated Morse (T.M.) form of interatomic potentials. (It may be pointed out that although, we present results on Co, the main conclusions of the paper are applicable to other transition metals also, as the D.O.S. in them are related to that of Co through a simple scaling). In Figs. 1 and 2 we have shown our earlier results ⁽⁴⁾ on the D.O.S. in H.S., L.J., T.M. and Morse potentials. In Fig. 2 we have also shown the D.O.S. in liquid Co, using Monte-Carlo

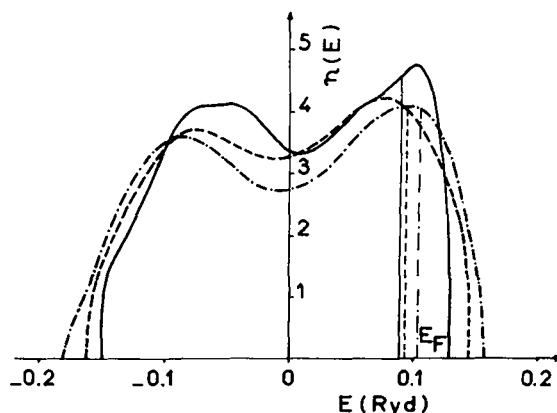


Fig. 1 : Density of d-states using H.S. (—), L.J. (---) and T.M. (-.-.-) models.

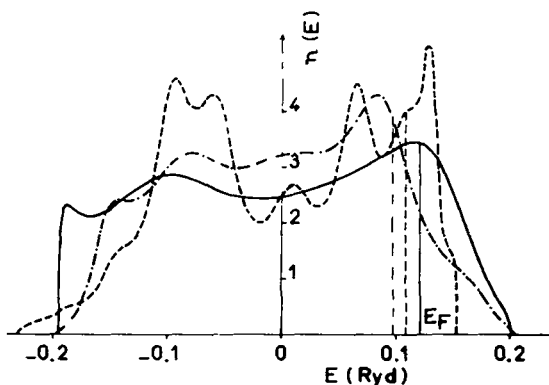


Fig. 2 : Density of d-states based on Morse model (—), Monte Carlo (-.-.-) and those in the FCC crystal (---).

generated atomic configurations with a repulsive coulombic form for the interatomic potential which gives a good description of the pair distribution function, $g(r)$, in liquid transition metals ⁽⁷⁾. It is clearly seen in the figures that all the models for the amorphous state and the Monte-Carlo result for the liquid show a double peak form for the D.O.S. This result is not surprising as we know that it is the repulsive part of the potential which mainly governs the structure of a system i.e. the structure is not too sensible to the attractive

part. As the electronic structure determines the attractive part of the energy or the potential, it is less sensitive to the structure. Nevertheless, though the main shape of the D.O.S. is not changed, we notice from Figs. 1 and 2 that as the potential is softened, the band-width increases. Also the fall in the density of states at the top of the band becomes less steep as the potential is softened. Before we explain these results, let us consider the density of the models. In Table I we have given the average atomic volume v_0 for the central core of 100 and 500 atoms in the various models used by us (the units are chosen so that the first peak position in theoretical $g(r)$ coincides with experiment (8)).

MODEL	ATOMIC VOLUME v_0 (\AA^3)	
	100 ATOM CORE	500 ATOM CORE
H.S.	12.9	12.8
L.J.	12.4	12.2
MORSE	10.6	12.6
T.M.	11.6	11.7
LIQUID Co(9)		12.7

Table I : Atomic volume in various models.

We see from the above table that as the repulsive core of the potential becomes softer, the atomic volume decreases and the system becomes denser, the particles are able to approach each other more closer. It is reflected in the first peak of $g(r)$ which becomes broader. This increases the bandwidth as well as decreases the steepness of the fall at the top of the band. Influence of the density on D.O.S. may become important at a local level. Indeed, substantial fluctuations can occur in the local $g(r)$. This will have effect on the local D.O.S. and as the first peak in the local $g(r)$ becomes stronger and sharper, the double peaked structure in the local D.O.S. becomes sharper⁽⁴⁾. We thus expect a change in the D.O.S. as one passes from the

bulk to the surface, since the local surroundings are highly changed. It is indeed the case.

Using the L.J. relaxed model we have calculated the local D.O.S. at various surface sites. In Fig. 3 we have shown the local D.O.S. on three surface

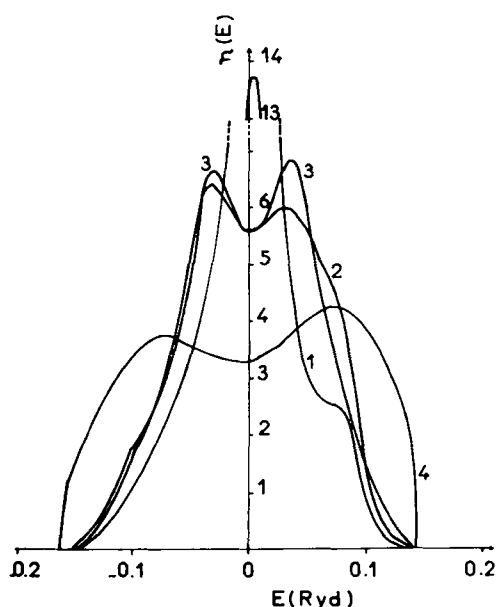


Fig. 3 : Density of d-states at surface sites (1, 2 and 3) compared to those in bulk (4).

sites 1, 2 and 3 having 5, 7 and 8 neighbours. It is seen that the surface atoms have D.O.S. with a narrow central peak or a weakly split double peak and a smooth tailing at the band edges. This can be attributed to a decrease in the coordination number as one passes from the bulk to the surface, which results in the occurrence of a resonant state due to the weak coupling of the surface atoms to the bulk. It is interesting to note that the above result is analogous to a similar phenomenon occurring in rough crystalline surfaces, studied by F. Cyrot-Lackmann et al⁽¹⁰⁾. This behaviour will surely affect the magnetic and chemisorptive properties of the amorphous metal surfaces. This will be discussed in a forthcoming paper.

Amorphous Co is a ferromagnetic metal and we wish to point out that by a simple prescription⁽⁴⁾,

one can build the ferromagnetic D.O.S. from the paramagnetic D.O.S. These are shown in Fig. 4 for the bulk ferromagnetic case and for the surface, assuming the surface magnetic moment to be the same.

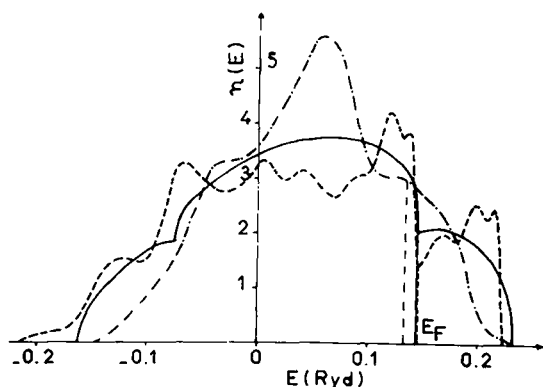


Fig. 4 : Density of d-states in ferromagnetic amorphous Co (—), at a surface site (---) and those in the HCP crystal (-.-).

Let us now briefly discuss the various properties directly related to the D.O.S. The difference, ΔE_c , between the cohesive energies of the crystalline and the amorphous phase gives an indication of their relative stability. We have found reasonable ΔE_c values of 0.41, 0.29 and 0.12 eV for the H.S., L.J. and T.M. models.

The bulk density of states can be used to study the electrical properties. Our calculated density of states at the Fermi level decrease by $\sim 25-30\%$ in going from amorphous to crystalline Co, which matches with the resistivity measurements which show a decrease of resistivity⁽¹¹⁾, dominated by d-effects in transition metals.

Finally, we would like to remark that a simple application of our calculated density of states in a B.C.S. formula can explain the variation of the superconducting transition temperature T_c along a transition metal series⁽¹²⁾.

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