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CHEMICAL SHORT-RANGE ORDER IN SIMPLE-METAL AND IN TRANSITION-METAL GLASSES*

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Résumé - Un calcul microscopique de l'ordre chimique à courte distance est présenté dans le cas d'alliages amorphes binaires (2 métaux simples ou 2 métaux de transition). La méthode repose sur une technique de pseudopotentiels pour les métaux simples, et un modèle d'Hamiltonien de liaisons fortes avec l'approximation des amas de Bethe pour les métaux de transition. Les hypothèses variationnelles thermodynamiques sont utilisées.

Abstract - We present microscopic calculations of the chemical short-range order in amorphous alloys of two simple metals or two transition metals. Our method is based on the pseudopotential technique for simple metals, on a model tight-binding Hamiltonian and the Bethe-cluster approximation for transition metals, and on a thermodynamic variational technique.

I - INTRODUCTION

After twenty years of structural investigations the question remains controversial wether there exists a pronounced chemical short-range order (CSRO) in metallic glasses and wether such an ordering enhances the glass-forming ability or not. It is true that the CSRO is very hard to measure (for recents reviews of the state-of-the-art see Steeb and Lamparter /1/ or Wagner /2/) - but a microscopic theory of CSRO seems to be an even harder task.

In principle one could proceed in two different ways: (a) Given an expression for the free energy as a function of the atomic coordinates, the equilibrium configuration is calculated by minimizing the free energy. (b) Given the interatomic forces, the structure of the glass is calculated using some computer-simulation algorithm (or - more conveniently - using some approximate analytical technique).

We all known that it is much harder to calculate interatomic forces than total energies from first principles. In fact only for the simple metals and their alloys reliable interatomic forces may be derived from pseudopotential theory /3/. In Sec.2 we recapitulate very briefly the calculation of interatomic pair potentials in binary simple-metal alloys and we show that a redistribution of the valence electron charges may result in a nonvanishing ordering interaction. For the liquid and the supercooled liquid phase, the partial pair correlation functions and static structure factors may then be calculated using a thermodynamic variational technique based on a reference system capable of simulating CSRO /4,5/ or a molecular dynamics calculation. A model for the amorphous structure is derived from the molecular dynamics (MD) liquid using a "quench"-procedure proposed by Weber and Stillinger /6/. This serves to check the variational procedure and to verify the ordering potentials. First results for Mg-Zn and for Ca-based glasses are presented.

The thermodynamic variational technique is particularly interesting, because it requires only the knowledge of the total energy and is not restricted to a pair-potential Hamiltonian. In Sec.3 we present a new thermodynamic variational technique based on a tight-binding representation of the electron states, which is applicable to transition metal alloys. First results for Ni-Ti glasses are presented.

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II - CHEMICAL SHORT-RANGE ORDER IN SIMPLE-METAL GLASSES

II - 1 - ORDERING POTENTIALS

The form of the interatomic potentials in binary alloys is strongly influenced by competing electron transfer mechanisms related to the electronegativity and electroneutrality principles /7/ - within the pseudopotential formalism these are reflected by orthogonalization and screening effects /3,5/. Upon alloying, elctrons flow into the direction of the more electronegative element (its orthogonalization hole is reduced on alloying). In the second step, electrons are allowed to rearrange themselves as to reduce potential energy gradients created by the charge transfer - this constitutes a second electron transfer mechanism opposed to the first one. The interatomic potentials are mainly influenced by the screening effect. Accumulation of screening charge in the core region of the electropositive ion is responsible for its "chemical compression", loss of local charge neutrality can lead to an enhanced interaction between the unlike atoms and hence to chemical ordering - see /5/ for a more detailed discussion. For our purpose it is most convenient to re-express the individual pair interaction in terms of a mean pair potential $\Phi_{NN}(R)$ coupling to the fluctuations in the mean number density, an ordering potential $\Phi_{cc}(R)$ coupling to the local concentration fluctuations, and a cross-term $\Phi_{Nc}(r)$. Fig.1 shows the pair potentials of Mg_7Zn_3 alloys - a positive $\Phi_{cc}(R)$ around the nearest neighbour distance indicates a small tendency to heterocoordination.

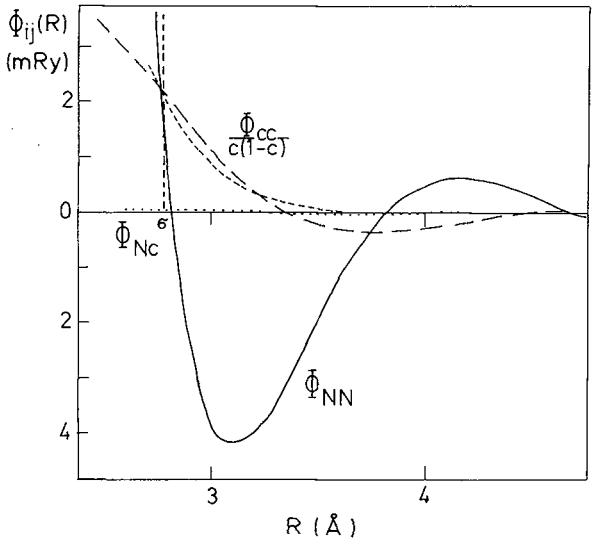

Fig.1
Interatomic potentials $\Phi_{NN}(R)$ (full line), $\Phi_{cc}(R)$ (dashed line), and $\Phi_{Nc}(R)$ (dotted line) for $Mg_{70}Zn_{30}$ alloys.
The short-dashed line shows the variationally determined Yukawa-type ordering potential, σ is the effective hard-sphere diameter.

II - 2 - THERMODYNAMIC VARIATIONAL APPROACH TO CHEMICAL SHORT-RANGE ORDER

For many simple liquids a reasonably accurate description of the structure and the thermodynamic properties may be derived from a thermodynamic variational approach - provided that a sufficiently realistic reference system is available. Very recently it has been shown that a system of charged hard spheres of equal diameters interacting by Yukawa potentials meets the requirements for an appropriate reference system: analytic solutions for the partial structure factors and for the thermodynamic functions are available and model the known trends in ordering liquid alloys quite well /8/. Fig.1 shows that the variationally determined model parameters (i.e. diameter of the hard spheres, strength of the ordering potential at hard contact, and screening constant) are realistic, from Fig.2 we learn that this simple model describes the ordering effects in liquid and in amorphous $Mg_{70}Zn_{30}$ quite well - for

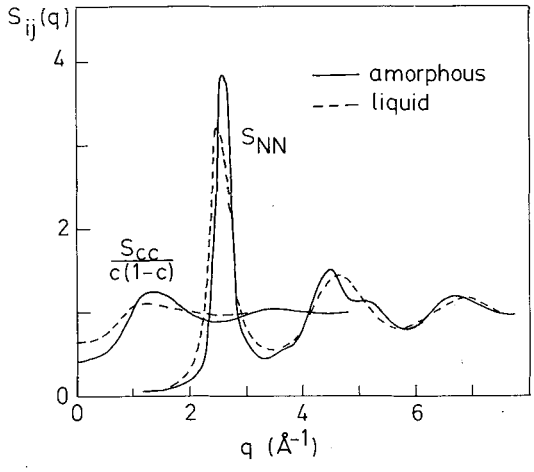

Fig.2 - Partial structure factors $S_{NN}(q)$ and $S_{cc}(q)$ of liquid and amorphous $Mg_{70}Zn_{30}$ (see text).

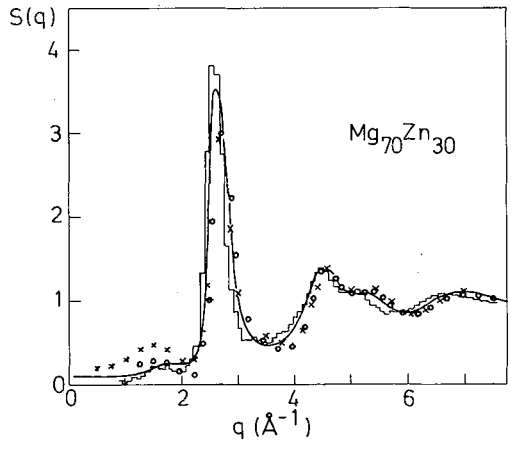

Fig.3 - Composite (X-ray weighted) static structure factor S(q) of amorphous $Mg_{70}Zn_{30}$: histogram - calculated using the molecular dynamic "quench", full line - variational calculation, crosses and circles - experiment /10/.

the amorphous state we had to assume that $S_{cc}(q)$ can be approximated by the results of the variational calculation for a supercooled melt just above the glass-transition, while $S_{NN}(q)$ and $S_{Nc}(q)$ are taken from an earlier cluster-relaxation calculation /9/.

II - 3 - MOLECULAR DYNAMICS STUDY OF CHEMICAL SHORT-RANGE ORDER

To verify the results of the variational technique, we have performed a molecular dynamics simulation of liquid and amorphous $Mg_{70}Zn_{30}$. A 800-particle cluster with periodic boundary conditions was used, the Newtonian equations of motion were solved using the Verlet algorithm with a time increment of 3×10^{-15} s. Classical dynamical trajectories of 10^4 time steps were generated to calculate properties of the alloy at each temperature. Momentum scalling was used to vary the kinetic energy and thus the temperature, after each scaling equilibration runs of at least 3×10^3 time steps were interposed. During the molecular dynamics run the atomic configurations were periodically mapped onto nearby potential minima. This mapping was achieved by instantaneously removing the kinetic energy and relaxing the systems configuration into the next potential energy minimum using a static energy minimization technique. We expect that a mapped configuration represents a good model for the amorphous structure. In Fig.3 we compare the composite (X-ray weighted) static structure factors derived from this molecular dynamics "quench" and from the variational calculation with experiment /10/ - a small prepeak indicates a weak degree of CSRO. From the partial pair correlation function we derive a Cargill-Spaepen short-range order parmeter of $\eta = 0.135$. These results confirm the validity of the variational procedure. Further details of the molecular dynamics calculations will be published elsewhere.

III - CHEMICAL SHORT-RANGE ORDER IN TRANSITION-METAL GLASSES

Progress in the modelling of amorphous tranition-metal alloys has been hampered by the fact that realistic interatomic potentials are not available - on the other hand it is relatively easy to calculate total energies for transition metal systems. Thus the variational procedure adopted for the simple metals seems to be an attractive tool for handling transition metals - the only difference is that the pair-potential Hamiltonian describing the simple metals has to be replaced by a tight-binding d-electron Hamiltonian which is more appropriate for transition metals.

For a given tight-binding Hamiltonian H, the equilibrium configuration is calculated by minimizing the variational expression

$$F < F_{HSY} - < H - H_{HSY} >_{HSY} = \frac{3}{2} k_B T + E_T(\varepsilon,\kappa) - T S_{HSY}(\varepsilon,\kappa) \quad (1)$$

with respect to the parameters ε(strength of the ordering potential at contact) and κ(screening constant in the Yukawa interaction) - the hard sphere diameter is fixed by assuming that a packing fraction of η=0.56 is representative of the alloy just above the glass transition temperature. The total energy $E_T(\varepsilon,\kappa)$ for a given configuration is calculated using the Cayley-tree method introduced by Falicov and co-workers /11/. The HSY-pair correlation function $g_{ij}(R)$ enter for example the expressions for the self energies Δ_A, Δ_B , in the Bethe-cluster approximation we have

$$\Delta_A = \frac{n\, c_A \int t_{AA}^2(R) g_{AA}^{HSY}(R)\, d^3R}{\mathfrak{z} - \varepsilon_A - \Delta_A} + \frac{n\, c_B \int t_{AB}^2(R) g_{AB}^{HSY}(R)\, d^3R}{\mathfrak{z} - \varepsilon_B - \Delta_B} \quad (2)$$

where the $t_{ij}(R)$ and ε_i are the transfer integrals and atomic energy eigenvalues respectively. For each configuration represented by given values for $\varepsilon$and κ, the shift of the energy band and the electron transfer are calculated self-consistently, the equilibrium configuration is determined by minimizing the free energy (1).
Our method is similar to earlier attempts to calculate CSRO in disordered systems /12/, which are also based on the Cayley tree method and a HSY-reference system. In this work however, the HSY-reference system was coupled to the tight-binding Hamiltonian by equating the spectrally defined transfer of band electrons and the electrostatic charges of the HSY-system. We have two good reasons not to follow this convention: first, the definition of the charges and of the screening in the HSY system is not unique (does the screening penetrate into the hard core or not ?, cf. the discussion in /8/). Second, it is well known that a spectral definition of the electron transfer can yield quite misleading results (it is known from band structure calculations on intermetalic compounds that to interpret orbital occupancies too literally as charge transfer can give results in direct contradiction to chemical common sense - for example charge transfer from Al to Li /14/). This method also excludes the conceivable solution of charge transfer without chemical ordering. The variational method avoids all these problems and provides a sound thermodynamic

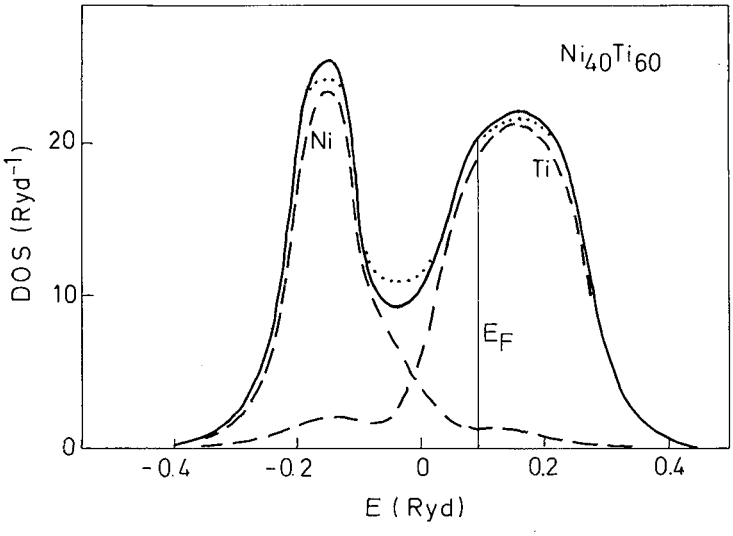

Fig.4 - Electronic density of states in amorphous $Ni_{40}Ti_{60}$: full line - including CSRO, dotted line - without CSRO, dashed lines - Partial DOS of Ni and Ti sites.

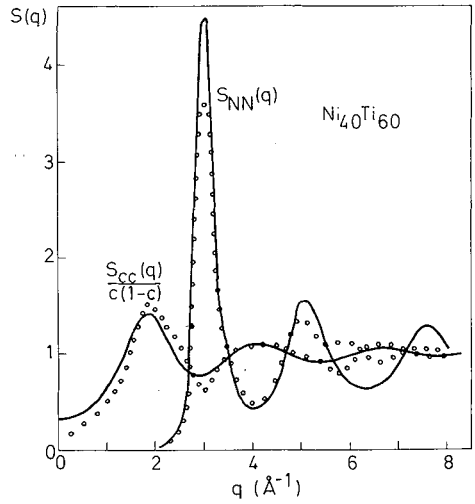

Fig.5 - Partial static structure factors $S_{NN}(q)$ and $S_{cc}(q)$ of amorphous $Ni_{40}Ti_{60}$. Full line - variational calculation , open circles experiment /13/.

basis for the calculation of CSRO. First results for amorphous $Ni_{40}Ti_{60}$ are shown in Figs. 4 and 5. The calculated electronic density of states shows the familiar shift of the d-band of the late transition metal. In the ordered equilibrium configuration the structure in the DOS is somewhat more pronounced - this is a consequence of a small electron transfer. The variationally determined partial static structure factors compare very well with those determined from isotope substitution experiments. To summarize: we have presented an appealingly simple and very promising method for calculating CSRO in liquid and amorphous alloys of simple- and of transition metals.

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