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ELECTRONS AND PHONONS IN METALLIC GLASSES

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ABSTRACT

This paper reviews recent advances in the calculation of electronic and vibrational states in metallic glasses. It starts with a brief discussion of the state of the art of structural modelling and the simplifications of the different modelling algorithms on the electronic and the vibrational properties. The various techniques for calculating the spectra of elementary excitations in the absence of translational symmetry (equation of motion method, recursion technique, multiple scattering cluster calculations, effective medium approximation) are critically reviewed. Exemplary applications of these methods to metallic glasses, involving comparisons with recent experiments on electron and phonon states are presented.

INTRODUCTION

Elementary excitations such as electrons, phonons, plasmons etc.. have been studied extensively in crystalline materials by both experimental and theoretical techniques. For amorphous solids the situation has not been nearly as thoroughly investigated nor as well understood. It is true that the difficulties start at a disconcertingly elementary level ; in a crystalline solid , the atomic coordinates are uniquely specified by the results of a neutron or X-ray scattering experiment. Given the atomic structure, we construct the Hamiltonian and the Bloch theorem teaches us how to diagonalize this Hamiltonian and to calculate the bands (dispersion relations of the elementary excitations), densities of state or other quantities that we are interested in. For an amorphous material, a scattering experiment yields only angular averages over interatomic distances (pair correlation functions). Thus the first task will consist in the construction of a structural model (a set of atomic coordinates) which should reproduce the main characteristics of the random geometric conditions for the interpretation of the diffraction data and serve as a starting point for the computation of the electonic, dynamic, magnetic etc... properties and their relevant spectral implications. The calculation of the spectra requires the construction of the Hamiltonian (but this can be done in the same fashion as for crystalline solids) and the choice of an efficient method for the diagonalization of the large Hamiltonian matrices without the use of Bloch's theorem. Since individual eigenvalues of the secular matrix have little significance, it is even preferable develop efficient means for the direct determination of the spectral functions and densities of state.

STRUCTURE AND FORCES

There are two essentially different ways for constructing amorphous model structures , the cluster relaxation method and the soft sequential addition technique (1). The cluster relaxation method starts from an idealized random structure constructed without reference to the interatomic interactions. The second step consists in the structural relaxation using certain interatomic potentials. In the soft sequential addition algorithm the interatomic forces are introduced from the very beginning : starting from a small irregular seed, atoms are added from random directions, their final sites are

determined by surface rather than bulk-effects. Hence it is necessary to proceed to a global relaxation of the cluster after its initial construction. This and the inherent complexity of a soft sequential addition algorithm have led to the fact that it is nowadays rarely used for the construction of models ment to represent specific amorphous substances, but it is still of fundamental interest. The main problems of the cluster relaxation approach are the choice of a starting structure and of the interatomic potentials and the compatibility of the two. There are two different techniques to produce a starting structure : one of them emphasizes the dense random packing of hard spheres (DRPHS) of different diameter (2,3), the other the chemical bonding which produces certain characteristic arrangements of atoms ("fundamental" or "molecular" unit) of high stability. Those unitsare then linked together to form a random network (4). Note that the two approaches are not necessarily radically different : certain chemical constraints (e.g. avoidance of certain types of nearest neighbours) may be added to the packing algorithms in the form of supplementary conditions. The next step is the determination of a set of interatomic potentials : only for simple metal alloys they can be constructed a-priori using pseudo potential techniques (5,6) (however, note the complications arising from the fact that these potentials are density dependent), for any other material empirical potentials of a Lennard-Jones or Morse-type must be used. Finally, starting structure must be relaxed under the action of the selected interatomic potentials by following some energy minimization algorithm (7,9). For systems with no or only little compositional ordering this allows indeed for an occurate reproduction of the diffraction data by a method which is entirely from first principles (Fig. 1).

For amorphous transition metal-metalloid alloys on the other side the existence of a strong chemical as well as topological short range order is by now firmily established. It is remarkable that models starting from rather different points (i.e. DRPHS) (3,10) or random stacking of trigonal prismatic units (4) achieve essentially the same degree of success, judging from the agreement with the experimentally determined partial radial distribution functions (11), see Fig. 2. In a recent study Fujiwara (12) has shown that the formation of trigonal prismatic clusters during the relaxation of a binary DRPHS model is due mainly to the difference in the atomic size and the short range interaction between the metal and the metalloid atoms. Evidently

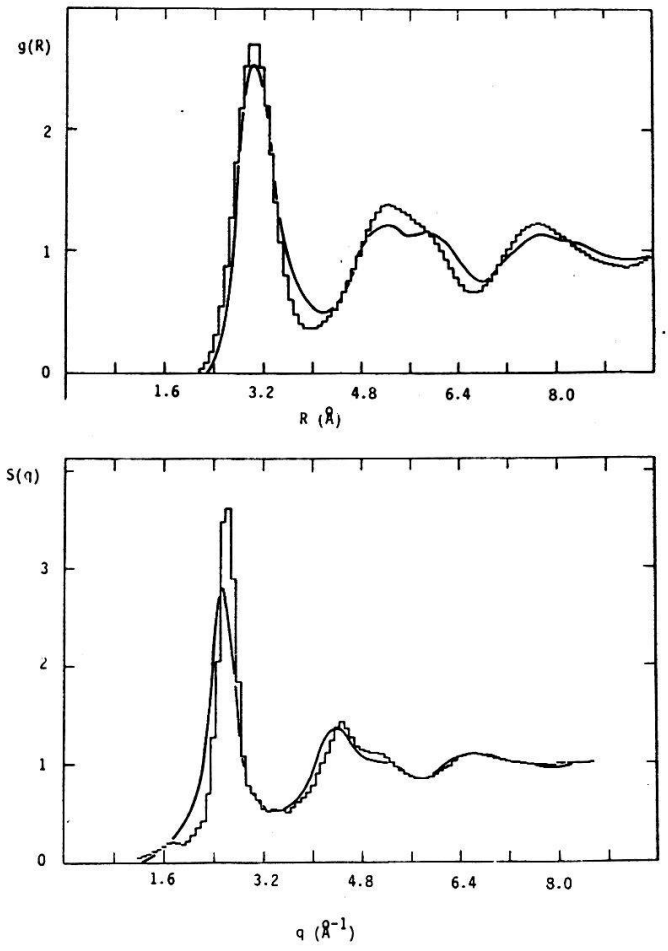

Fig. 1 : Composite (neutron weighted) interference function S(Q) and pair correlation function g(R) for the metallic glass $Mg_{70}Zn_{30}$. Full lines experiment at T = 273 K (Mizoguchi, unpublished), histogram theory (based on pseudo potential derived interatomic forces, including Deby-Waller damping resp. thermal broadening calculated for T = 273K, after ref. 9.)

one of the goals of an electronic structure calculation for these materials consists in providing a microscopic justification and possibly an improvement of this type of interatomic potential.

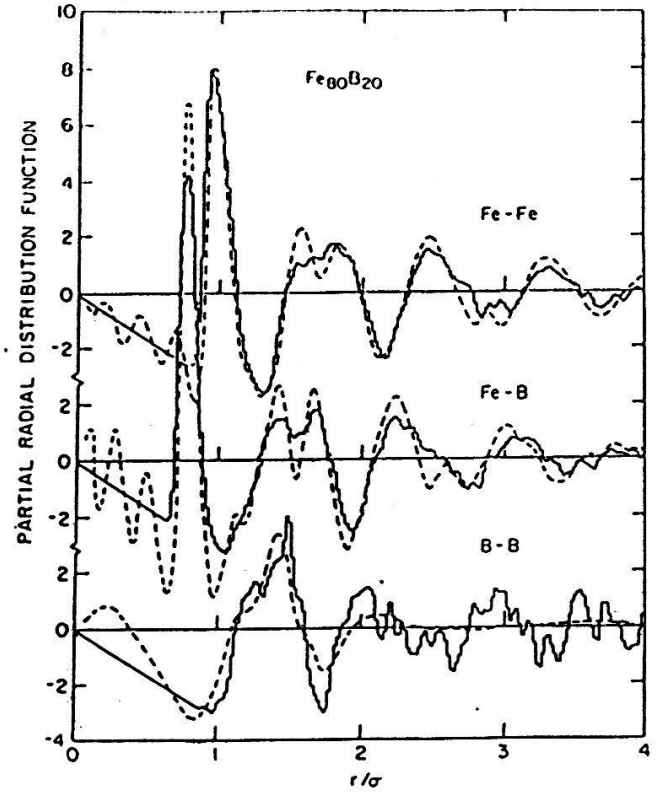

Fig. 2 : Comparison of the experimental partial radial distribution functions for amorphous $Fe_{80}B_{20}$ (dashed lines, after ref. 11) with the model structure (histogram, ref. 10).

PHONONS

Given a model structure and a set of interatomic potentials, the vibrational spectrum may be calculated either by a molecular dynamics simulation or by the recursion (13) or the equation-of-motion (14) techniques. The latter computes the vibrational density of states (DOS) projected onto an initial state Ψ in the form of a Fourier integral over the time dependent displacement displacement correlation fonction, i.e.

$$n_\Psi(\omega) = \mathrm{Re}\,\frac{1}{\pi}\int_0^T e^{i\omega t}\sum_{i,\alpha} u_{i\alpha}(t)\,u_{i\alpha}(0)\,f(t)\,dt \qquad (1)$$

Here the $u_{i\alpha}(t)$ are the α components of the time-dependent of the displacement of the i-th atom from its equilibrium position, the $u_{i\alpha}(t = 0)$ define the initial state ψ, f(t) is a damping function introduced to minimize the effect of the truncation of the Fourier integral at the finite time. The $u_{i\alpha}(t)$ are determined by integrating the Newtonian equation of motion numerically by a Runge Kutta or predictor-corrector algorith (15). The recursion method works directly in the energy representation, the projected DOS is given by the imaginary part of the diagonal matrix element of the resolvent $(\omega^2 - D + i\delta)^{-1}$, i.e.

$$n_\psi(\omega) = -\frac{2\omega}{\pi} \lim_{\delta \to 0} \mathrm{Im} \langle \psi | (\omega^2 - D + i\delta)^{-1} | \psi \rangle \qquad (2)$$

where D is the real space dynamical matrix.

The recursion method than proceeds by a transformation to a new basis in which the dynamical matrix is tridiagonal. The inversion of the tridiagonal matrix $(\omega^2 - D)^{-1}$ finally produces a continued fraction representation for the spectrum. Note that both the truncation of the infinite continued fraction and the termination of the Fourier integral (1) introduces a finite resolution in the spectrum (see Ref. 9,17 for details). The dispersion of collective excitations may be investigated by means of neutron inelastic scattering (16). If the initial state ψ is a plane wave with wave vector $\vec{q}$ and polarisation vector e, the calculated spectrum $n_\psi(\omega)$ represents a spectral function $S_{\alpha\beta}(Q,\omega)$ of the dynamical Hamiltonian. More specifically we calculate the spectral functions $S_{NN}(Q,\omega)$ of number density fluctuations if all the atoms are displaced initially or, if only the atoms of a particular species A are displaced, the partial spectral function $S_{AA}(Q,\omega)$. By fixing the orientation between $\vec{Q}$ and $\vec{e}$, longitudinal as well as transverse excitations may be investigated (however, only longitudinal excitations may be probed experimentally). The inclastic neutron scattering law $S(Q,\omega)$ may be calculated from the spectral functions, superposing them with the appropriate weighting factors (neutron scattering length, partial Debye-Waller factors, masses-see (9) for details) and multiplying with the thermal occupation factors. In Fig. 3 the neutron scattering law for the metallic glass $Ca_{70}Mg_{30}$ (for which the interactomic forces may be derived from pseudo potential theory), calculated using the recursion method (9) is compared with experiment (16).

The agreement is generally very good, except for the high energy tail of the experimental spectra which stems for hydrogen impurities in the sample. The most striking feature of the spectra is the shift of the peak in $S(Q,\omega)$ to very low energies for momentum transfers around $Q \simeq Q_p$, the wave vector where the static structure factor has its first maximum. The dispersion law for collective density fluctuations is shown in more detail in Fig. 4.

Analytical calculations have shown that the dispersion minimum near Q_p arises from a process which is best described as a "diffuse Umklapp scattering", the relatively sharp peak of the static structure factor acts like a smeared out reciprocal lattice vector (18).

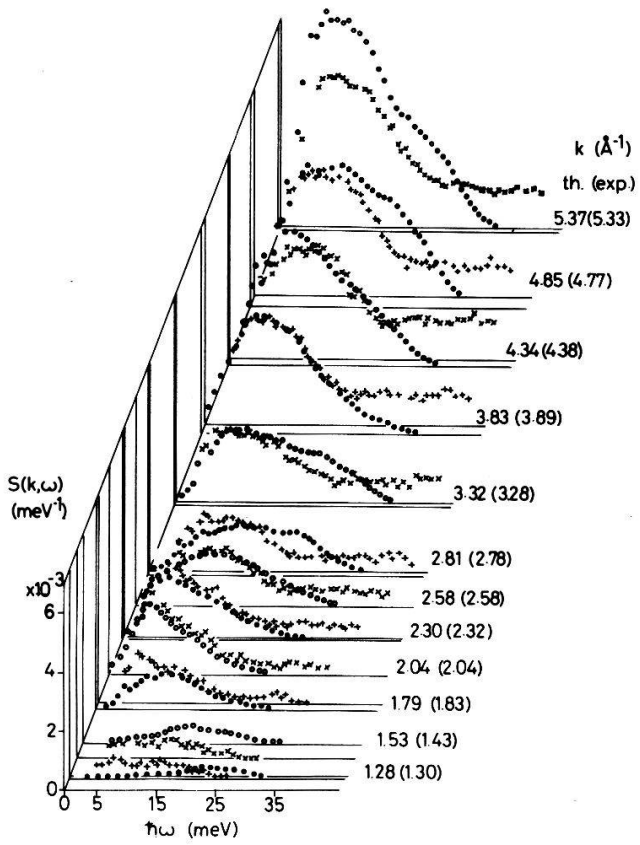

Fig. 3 : Inelastic neutron scattering law for the metallic glass $Ca_{70}Mg_{30}$: crosses experiment (Suck and Rudin (16), circles calculation (9).

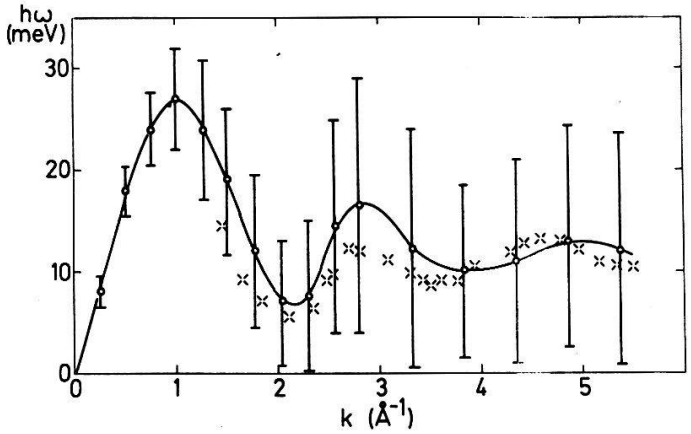

Fig. 4 : Dispersion law per propagating collective excitation in glassy $Ca_{70}Mg_{30}$. Circles pear positions in the calculated S(K,ω), bars show the width at half maximum, crosses - peaks in the measured spectrum.

For Ca-Mg alloys the mass and force constant differences are relatively small. Therefore the vibrational bands relevant to the two components

largely overlap and the two-component nature of the material doesn't show up in the neutron scattering law. The mass and force constant disorder is much larger for Mg-Zn glasses. The spectral functions of Mg and Zn vibrations in amorphous $Mg_{70}Zn_{30}$ are remarkably different : the Mg states display the by now familiar dispersion relation, although the large width of $S_{MgMg}(Q,\omega)$ for small Q and the shoulder appearing near $Q \simeq Qp$ indicate some degree of interaction with the Zn vibrations. The Zn vibrations show nearly no dispersion and are centred at low energies. For both longitudinal and transverse vibrations the dispersion relations for two distinct modes corresponding to the acoustic and optic modes in the crystal can be determined. At very long wavelength, these modes correspond to collective density and concentration fluctuations, at short wavelength they can be identified with the incoherent vibrations of the two atomic species. For longitudinal excitations the predicted dispersion law can be compared with recent neutron inelastic scattering experiments and good agreement is found (17).

In summary we find that the vibrational states in the glassy and in the polycrystalline materials are surprisingly similar. Studies of the interrelation between the local structural parameters and the local vibrational DOS (9,19) reveal the origin of the remaining difference and explain the relaxation effects observed in the vibrational spectrum.

ELECTRONS

The methods for the calculation of the vibrational spectrum sketched in the last paragraph are equally applicable to a calculation of the electronic spectrum, replacing the dynamical Hamiltonian by an electronic Hamiltonian based either on a tight-binding or muffin-tin orbital approach (20,21). Another possibility is to represent the amorphous material by a set of small irregular clusters (usually less than twenty atoms). At the expense of this drastic restriction one gains the possibility of doing realistic calculations for the atoms retained (22,23). Electronic band structure calculations on hypothetical crystalline compounds of appropriate composition have also been useful in the interpretation of electronic spectra of amorphous alloys (24). The very fact that this is possible already shows that the topological disorder is relatively unimportant. Very recently, the first application of the effective medium approximation (EMA) to metallic glasses has

been presented (25).

Amorphous transition metal-metalloid alloys have been most widely investigated (20,21). The results show : (i) The strong s-p hybridization characteristic of the electronic structure of the pure metalloid (B,Si,P..) is broken in the binary alloy. The s- electrons of the metalloid form a quite narrow band situated well below the Fermi-energy, (ii) The p electrons of the metalloid strongly interact with the d electrons of the transition metal. This results in a narrowing of the d band as compared to the pure transition metal and in a large bonding-antibonding splitting of the metalloid p-states (Fig. 5). This picture is well confirmed by photo-emission and soft X-ray measurements : the principal feature of the spectrum is dominated by the transition metal d-band, the antibonding p- states influence the form of the spectrum at the Fermi edge, the structures observed at the low energy tail of the main peak stem from the bonding p-states.

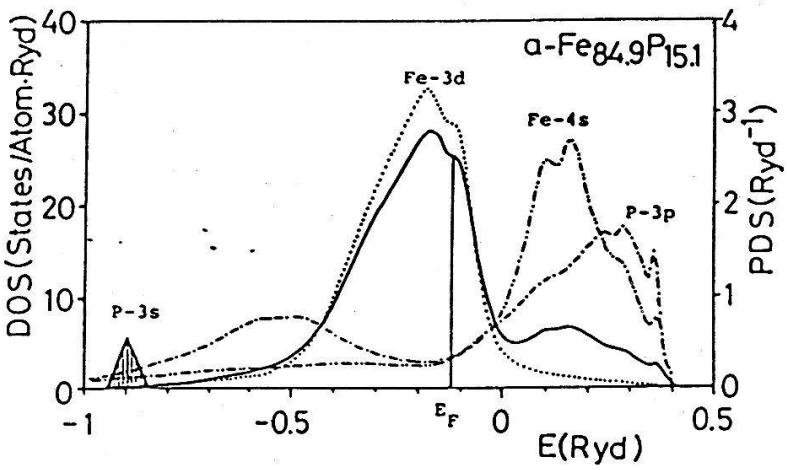

Fig. 5 : Electronic density of states for amorphous $Fe_{85}P_{15}$ (after Fujiwara (21)), full line total DOS, partial DOS as indicated.

Again the calculations reveal an astonishing similarity between the spectra of the crystalline and the amorphous phases. Attempts have been made to study the influence of different models of the atomic structure on the electronic spectrum, but the possibility of extracting topological information of any quality seems to be remote.

The electronic spectrum of amorphous alloys between an early (T_E) and a late (T_L) element of the transition metal series is characterized by a large shift of the d band of the T_L component to larger binding energies whose magnitude depends on the group number difference. Recursion calculations (26), the EMA (25), cluster calculations (22,23), and band structure calculations

for hypothetical compounds with CsCl, CuAu, or Cu_3Au structures (27) all emphasize the importance of a hybridization of the d states of the two components. The cluster calculations in particular demonstrate the predominant influence of the local chemical order on the electronic structure as opposed to the small influence of the topological disorder.

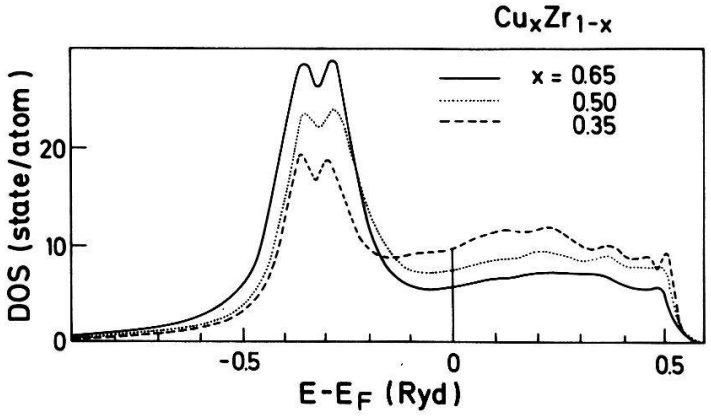

Fig. 6 : Calculated electronic density of states for Cu-Zr glasses (after Fujiwara (26)).

Only very recently the first results for the electronic structure of simple metal glasses became available. Low temperature specific heat measurements (28), the investigation of the Compton profile and of the angular correlation of the position annihilation radiation (29) all point to a completely free electron like character of the electronic structure of amorphous $Mg_{0,70}Zn_{0.30}$. Therefore it was very surprising that the UPS and SXS spectra measured on amorphous Ca-Al alloys of various concentrations seemed to indicate a strong deviation from the free-electron character (24). Again the spectrum of the amorphous alloy is characteristically similar to that of the crystalline intermetallic compound $CaAl_2$ (cubic Laves phase) but different from that of pure Al ((30), see Fig. 7). The SXS spectra of pure Al and of $CaAl_2$ are well explained by a linearily screened pseudo potential. In agreement with band-structure calculations on hypothetical crystalline Ca_3Al (Cu_3Au type) and CaAl (CsCl type) alloys (24) it is found that the dominant effects are (i) the incipient population of the Ca-d band and (ii) a splitting of the s-p band, most prononced on the Al-sites, whereas the s- and p states of Ca contribute equally to both peaks of the valence bands. The reduced hybridization of the Al s and p states stems from the reduced overlaps from nearest neighbour like-atoms, the Ca orbitals on the other side are subject to strong hybridization because of the high coordination number for unlike neighbours

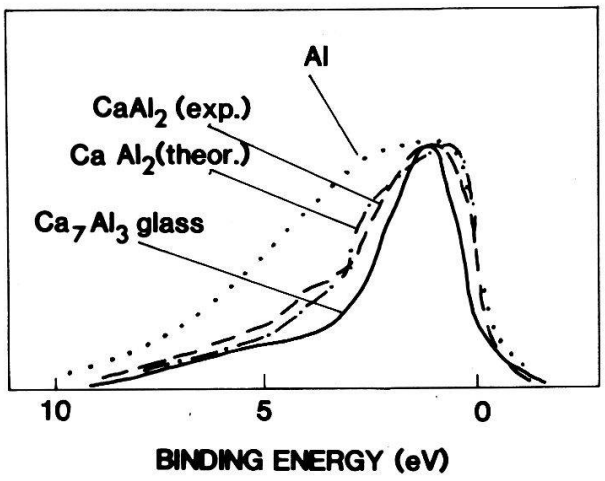

Fig. 8 : The soft X-ray emission band (3p 1s transition) for Al in the pure metal (dotted) in the metallic glass $Ca_{70}Al_{30}$ and in the intermetallic compound $CaAl_2$ (dashed experiment, dot-dashed theory).

and the decrease of the Ca-Ca distances on alloying (6).

CONCLUSIONS

The results obtained up to now emphasize the importance of local factors in determining the properties of elementary excitations in glasses : inspite of the absence of long-range translational invariance, diffuse Umklapp processes characterize the phonon spectrum, and the remaining differences in the vibrational DOS of the glass and the polycrystal may be traced back to a wider spectrum of variations of the local structural parameters in the glass. The electronic spectrum of metallic glasses and of their corresponding crystalline alloys is characterized by a interaction between the orbitals of the two constituents : p-d hybridization in transition metal-metalloid glasses, d-d hybridization in intertransition metal glasses, and s,p - s,p interaction in simple metal glasses ; the long range order influences only minor detailsof the electronic structure. If the aim of the electronic investigation was to reveal the origin of the stability of metallic glasses, the result must appear disappointing. On the other hand the systematic investigation of rapidly quenched alloys has revealed many new and often unexpected aspects of the electronic structure. Our improved knowledge should yield to refined models of the interatomic interactions as a first step towards the self consistent calculation of the atomic and the electronic structure.

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