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The electronic structure of liquid metals

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Abstract. We present first-principles calculations of the electronic structure of molten simple and transition metals.

The success of Ziman's diffraction model in rationalizing a seemingly diverse mass of experimental data has led to the deep-rooted belief that the electronic density of states of liquid metals is free-electron-like. The discovery that the absence of long-range order is not in itself sufficient to preclude the possibility of strong structures (even gaps) in the electronic spectrum has not shattered this simplistic view. It is true that until recently the state-of-the art of both theory and experiment was not sufficiently advanced to challenge the free-electron model seriously. This situation is now gradually changing: accurate photoemission studies [1–3] have demonstrated that strong deviations from a free-electron DOS exist in the heavy polyvalent liquid metals; even the photoemission intensity of liquid Na has a rather unexpected shape [2].

For a liquid a diffraction experiment yields only statistical information on the distances between pairs of atoms (the pair correlation function) and this is much less information than necessary for an accurate calculation of the electronic structure. Therefore any attempt to calculate the electronic structure has to start with the calculation of the liquid structure.

In our studies [4–7] we adopted the following strategy.

(1) Calculate the effective interatomic interactions using pseudopotential theory for the simple metals [8] and using a hybridized nearly-free-electron tight-binding-bond (NFE–TBB) approach for transition metals [9, 10].

(2) Calculate the liquid structure using molecular dynamics. Simulations for large ensembles allow a reliable comparison with experimental structure data, simulations for small ensembles provide the data base for the electronic structure calculations.

(3) The electronic structure is calculated self-consistently for a disordered arrangement of 50–70 atoms (representing an instantaneous configuration of liquid) in a periodically repeated 'supercell'. We have shown that both minimum-basis-set methods such as the linearized muffin-tin-orbital (LMTO) method [5, 6, 11] and plane-wave basis methods such as dynamical simulated annealing (DSA) [12] can be used quite efficiently for s,p-bonded systems, but only the LMTO supercell technique can be used for d-bonded metals.

(4) Calculate the photoemission intensity [13, 14].

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It is true that this technique falls short of the ultimate goal of achieving self-consistency between the atomic and the electronic structure. This is possible only within the framework of the density-functional molecular dynamics technique proposed by Car and Parinello [15–18] which combines the conventional MD for the ions with the DSA equations of motion for the electronic degrees of freedom through quantum-mechanical forces calculated via the Hellmann–Feynman theorem. This technique is computationally more expensive in computer time by at least a factor of 10^2 than the scheme sketched above.

We confirm the arguments formulated by Hafner and Heine [19] for the crystalline and by Hafner and Kahl [20] for the liquid structures: the complex structures of Zn, Cd, Hg, Ga, In, Si, Ge and Sn, but also those of the liquid semiconductors like As [21] and Te [22] result from the modulation of the random packing of atoms by the Friedel oscillations in the effective interatomic interactions. In the heavy elements (Tl, Pb) these oscillations are damped out, partly through relativistic effects, and this determines the return to close-packed structures. Even for the liquid semiconductors As and Te, coordination numbers, bond distances and bond angles are predicted in reasonable agreement with experiment and with the *ab-initio* simulations. Substantial differences appear only in four-body correlations (average height of the trigonal pyramids in l-As [17], distribution of the dihedral angles in l-Se and l-Te. [18, 23]).

For the electronic structure, the results can be summarized as follows [4–7] (see figure 1).

(1) For Li and Be we find a strong reduction of the width of the occupied band and pronounced structure-induced minima in the DOS. This is a consequence of the strong p component of the electron-ion potential.

(2) The DOS of the elements from Na to Si is close to the free-electron parabola.

(3) s–d hybridization and the relativistic lowering of the d states relative to the s states induce strong deviations from a free-electron behaviour in the DOS of the liquid alkaline earth metals. l-Ba is found to be a transition metal with about 0.74 d-electrons/atom.

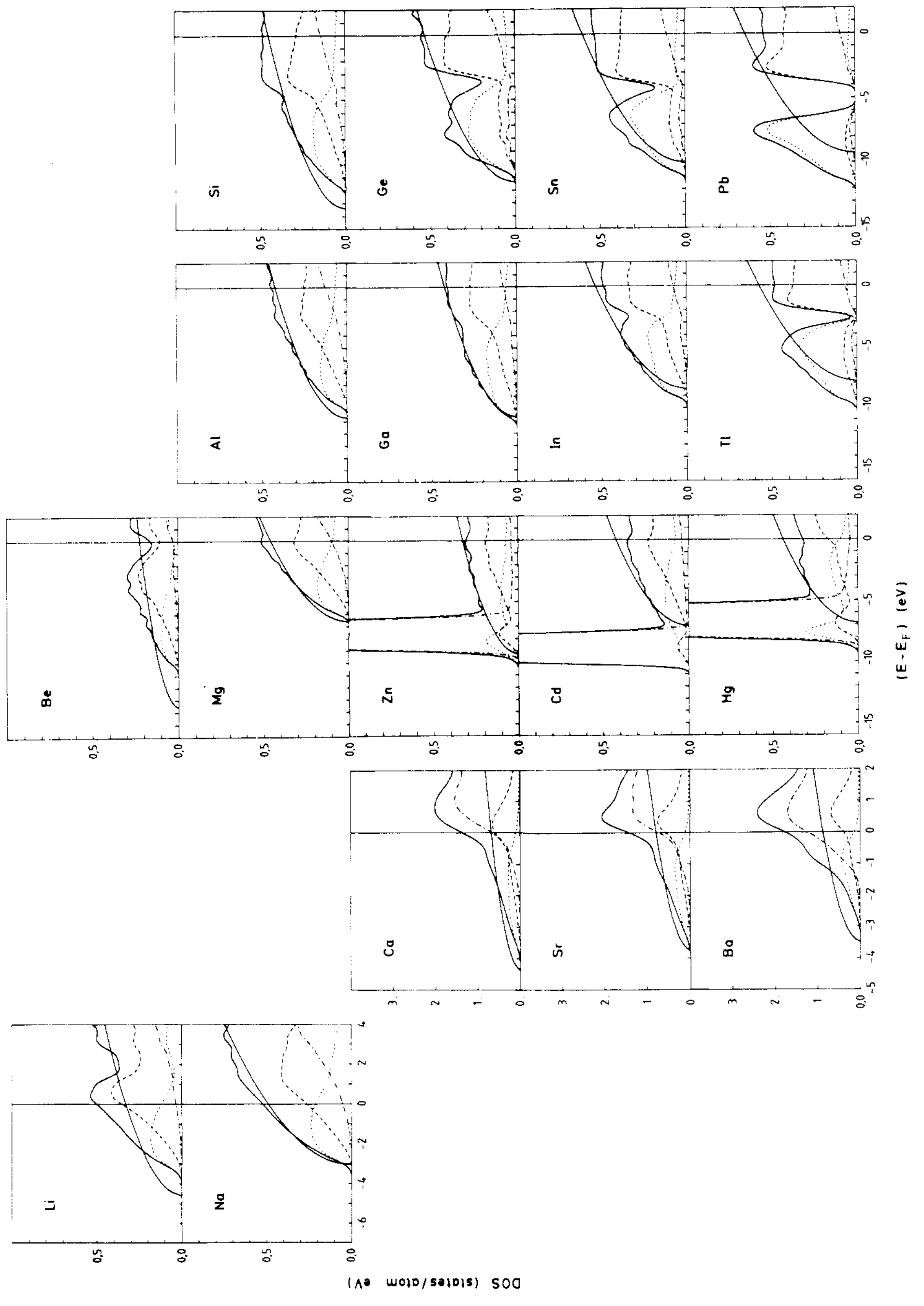
(4) In the IIb elements Zn, Cd, and Hg we find a progressive reduction of the DOS at E_F compared to the free-electron value, in agreement with the prediction of the Mott model for liquid mercury.

(5) In liquid In and Tl we predict deep pseudogaps 2–3 eV below E_F, in close analogy with the electronic structure of the crystalline metals. On the other hand the marked differences in the DOS of crystalline α-Ga and l-Ga reflect the change in the local atomic structure [7].

(6) In l-Si, Ge, and Sn the absence of strong angular correlations leads to a breakdown of sp^3 hybridization. In l-Ge, Sn, and Pb relativistic bonding effects lead to a formation of a pseudogap (a real gap in the case of l-Pb) separating the s and p states. In l-Ge this effect is enhanced by the low coordination number and by a penetration of the 4s orbitals into the 3d core.

(7) In the liquid semiconductors the correct description of the four-body correlation turn out to be essential for the formation of the gap at E_{F} [12, 17, 18, 23].

Figure 1. (Opposite) Electronic density of states of the liquid simple metals. Full curve, total DOS; dotted curve, s states; broken curve, p states; chain curve, d states. The free-electron parabola is shown for comparison.


Li
Na
Ca
Sr
Ba
Be
Mg
Zn
Cd
Hg
Al
Ga
In
Tl
Si
Ge
Sn
Pb
0,0
0,5
0
1
2
3
-15
-10
-5
0
-6
-4
-2
2
4
-5
-4
-3
-2
-1
1
2
(E - E_F) (eV)
DOS (states/atom eV)

(8) A quantitative discussion of the shape of the spectra is possible only if the partial photoionization cross-sections are calculated as a function of the binding energy of the electron and the energy of the exciting photon [13, 14]. This results in excellent agreement between theory and experiment [4–7].

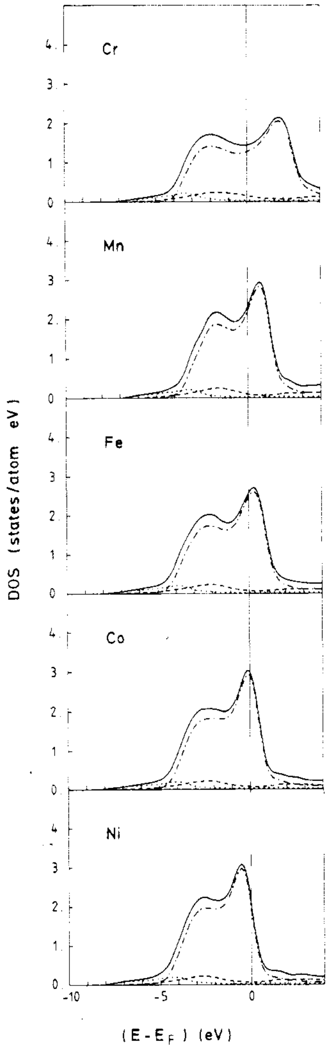


Figure 2. Electronic density of states of liquid 3d transition metals. Symbols as in figure 1.

The same tools can also be applied to liquid transition metals. The interatomic interactions are determined by strong covalent bonding forces mediated by the d-electrons and soft repulsive forces arising from the internal pressure arising from the more extended s states. MD simulations describe their liquid structure reasonably well [9]. The DOS of five molten 3d metals from Cr to Ni calculated using the LMTO supercell method are summarized in figure 2. The double-peak structure shows that the characteristic $t_{2g} - e_g$ splitting is preserved on melting. The gross features are in agreement with the measured soft-x-ray spectra [24], but the resolution of the experiment is not sufficient to permit a critical analysis of details.

To conclude, we have presented detailed results for the atomic structure, electronic DOS and photoemission spectra which have been obtained by methods that are essentially rigorous and derived from first principles. These techniques are readily generalized to binary alloys. Results for such alloys will be reported soon.

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