SHORT-RANGE ORDER OF LIQUID AND AMORPHOUS TRANSITION-METAL ALLOYS

Ch. Hausleitner, J. Hafner

HAL Id: jpa-00250626
https://hal.science/jpa-00250626

SHORT-RANGE ORDER OF LIQUID AND AMORPHOUS TRANSITION-METAL ALLOYS

Ch. HAUSLEITNER and J. HAFNER

Institut für Theoretische Physik, TU Wien, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria

Abstract: We present molecular dynamics simulations of liquid and amorphous transition-metal alloys based on quantum-mechanically derived interatomic forces. Using the interatomic potentials calculated within the hybridized nearly-free-electron tight-binding-bond (NFE-TBB) theory we construct models for $Ni_x TM_{1-x}$ (TM = Y, Zr, Nb, Ti, and V) glasses. We show that a clear trend from trigonal-prismatic to polytetrahedral local order and from strong to moderate chemical order exists in the series Ni-Y, Zr, Nb and with increasing Ni-content within a given system. These realistic structure models can be used also as a basis for selfconsistent supercell calculations of the electronic structure. Preliminary results are presented.

Introduction

The atomic structure of liquid and amorphous transition metals and alloys has been a subject of intense research for many years [1,2]. Several distinct glass-forming alloy families have been established [3]-[5]: (a) the transition-metal – metalloid systems (e.g. Fe-B or Ni-P), (b) the inter-transition-metal glasses (e.g. Ni-Zr or Fe-Ti), and (c) the simple-metal glasses (e.g. Mg-Zn or Ca-Al). Whereas for the simple-metal glasses of type (c) quite successful modelling studies using molecular-dynamics (MD) and potential-energy-mapping techniques [6,7] can be based on interatomic force fields derived from pseudopotential perturbation expansions [8,9], the situation is entirely different for the metallic glasses of type (a) and (b). For the metal-metalloid alloys the remarkable coincidence between the formation of glassy alloys and the formation of crystalline intermetallic compounds has led to the development of stereochemically defined models [10]. For the much more complex inter-transition-metal glasses of type (b) attempts to build structural models have been severely limited by the lack of reliable interatomic potentials.

Recently different theoretical attempts to this field have been made, like generalized pseudopotential perturbation theory, embedded-atom potentials or effective-medium-theory [11]. The problem with these methods is that either the interactions are too complex to be really useful in MD simulations or they encounter serious difficulties when applied to the transition metals with a half-filled d-band. Very recently a new bond-order approach to interatomic interactions has been proposed [12]. In this approach the covalent bond energy is written as the product of the transfer integral $h(R_{ij})$ between atoms located at a distance R_{ij} and the bond order Θ_{ij}. The bond order Θ_{ij} is defined as the difference between the number of electrons in the bonding $\frac{1}{\sqrt{2}}(\mid \varphi_i > + \mid \varphi_j >)$ and in the antibonding states $\frac{1}{\sqrt{2}}(\mid \varphi_i > - \mid \varphi_j >)$. Pettifor [12] has developed a many-body expansion for the bond order and calculates the bond order for crystalline materials with a recursion method approach. This technique requires the atomic positions to be known whereas in our case the liquid or amorphous structure is just what we want to derive from interatomic forces.

Here we present a novel hybridized nearly-free-electron tight-binding-bond (NFE-TBB) approach to interatomic forces in disordered transition-metal alloys. Our basic assumption is that the total energy may be divided up into contributions from s- and d-electrons:

$$E_{tot} = E_s + E_d \qquad (1)$$

The s-electron contribution is treated in pseudopotential perturbation theory [8,9] and the d-electron energy E_d is treated using TBB-theory. The bond order is calculated for a Bethe-lattice reference system. For the pure metals this leads to interatomic forces which are essentially equivalent to those derived from second-moment expansions [13,14]. For the alloys it turns out that the bond order depends very sensitively on the form of the partial density

of states (DOS). As the DOS of an AB-alloy changes from a common band to a split band form (reflecting a trend from small to large differences in the group number of the constituents), the variations in the bond orders lead to a change in the pair forces from a set of additive pair potentials to non-additive pair potentials with strong attractive short-range interactions in unlike-atom pairs. This leads to a strong topological and chemical short-range order in the atomic structure. Finally our computer generated structural models can be used for a selfconsistent supercell calculation of the electronic structure [15,16].

Hybridized NFE-TBB approach to interatomic forces

Based on density-functional theory Sutton et al [17] have shown that the total energy of a d-electron system may be written within a TBB approximation as

$$E_d = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} \Phi_{d,rep}(R_{ij}) + E_{d-bond} \tag{2}$$

where $\Phi_{d,rep}(R)$ is a repulsive pair interaction provided by the electrostatic, exchange-correlation, and non-orthogonality contributions to the total energy. The covalent bond energy E_{d-bond} is given by (assuming only one atomic orbital per site)

$$E_{d-bond} = \sum_i \int^{E_F} (E - E_{d,i}) n_i(E) dE$$

$$= E_{d-band} - \sum_i N_{d,i} E_{d,i} \quad . \tag{3}$$

E_{d-band} is the band energy (local DOS $n_i(E)$), $E_{d,i}$ is a reference energy equal to the free atom eigenvalue $\epsilon_{d,i}$ shifted by a crystal field and a non-orthogonality term. In eqn. (2), the on-site terms $\sum_i N_{d,i} E_{d,i}$ have been grouped with the ionic and double-counting terms. The main advantage of the bond energy concept is that it avoids problems related to charge-selfconsistency on alloying. In this case changes in the charge densities are not first-order and the corresponding shifts $\Delta E_{d,i}$ in the site-diagonal energies must be treated in *all* contributions to the binding energy. This is difficult when the electrostatic and double-counting terms are approximated by an empirical pair interaction. A simple way to solve this problem is to adjust the atomic levels until each site is charge-neutral [12]. This leads to a first-order change of the band energy of $\sum_i N_{d,i} \Delta E_{d,i}$ which must be cancelled according to the local force theorem of Pettifor [18] and Andersen [19], by an opposite change in the double-counting terms. Pettifor [12] shows that

$$\Delta E_{d,bond}|_{\Delta N_{d,\alpha=0}} = \Delta E_{d-band}|_{\Delta E_{d,\alpha=0}} \tag{4}$$

thus the bond energy with local charge neutrality satisfies the force theorem, since the site-diagonal energies do not appear explicitly. In the next step we want to break the bond energy into contributions from individual pairs of bonds. To do that we write the bond energy in terms of the Green's functions $G_{ij}(E)$ of the one-band TB-Hamiltonian as

$$E_{d-bond} = -\frac{1}{\pi} \sum_i \int^{E_F} (E - E_{d,i}) Im G_{ii}(E) dE$$

$$= \sum_{\substack{i,j \\ i \neq j}} h(R_{ij}) \left[-\frac{1}{\pi} \int^{E_F} Im G_{ij}(E) dE \right]$$

$$E_{d-bond} = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}} h(R_{ij}) \Theta_{ij} \tag{5}$$

with the bond order Θ_{ij}

$$\Theta_{ij} = -\frac{2}{\pi} \int^{E_F} Im G_{ij}(E) dE \tag{6}$$

expressed in terms of the imaginary part of the off-diagonal Green's function. Formally eqn. (5) for the bond energy looks like a sum over bonding pair interactions

$$\Phi_{d,bond}(R_{ij}) = h(R_{ij}) \Theta_{ij} \tag{7}$$

but the bond order depends on the surrounding atomic environment. The calculation of the Green's function requires an appropriate reference configuration. Chosing a Bethe-lattice reference system, the Green's function

can be calculated using renormalized perturbation theory [20]. Restricting to nearest neighbours interactions only (coordination number Z) we get a closed set of equations for the Green's functions [21]

$$G_{ii}(E) = \frac{1}{E - E_{d,i} - \Delta_i} \qquad (8.a)$$

$$\Delta_i(E) = ZhS \qquad (8.b)$$

$$G_{i0}(E) = SG_{i-1,0}(E) = S^i G_{00}(E) \qquad (8.c)$$

with the self energy Δ_i and the transfer matrix S determined by the solution of the equation

$$S = \frac{h}{E - E_{d,i} - ZhS} \qquad (9)$$

Eqns. (6) to (9) completely determine the bond order potential $\Phi_{d,bond}$. The average canonical transfer integral $h(R_{ij})$ is determined by a second moment approximation and fitted on the canonical bandwidths of Andersen and Jepsen [22]. For a fixed nearest neighbour distance (and hence a fixed transfer integral) we find $\Phi_{d,bond} \propto \Theta \propto 1/\sqrt{Z}$ and hence $E_{d-bond} \propto \sqrt{Z}$ as expected from a tight-binding approach [13,14]. For the repulsive d-potential $\Phi_{d,rep}(R_{ij})$ we take the expression of Wills and Harrison [14] who showed that it may be modelled as $C_{d,rep}/R_{ij}^8$.

The TBB-approach restricted to the nearest neighbours is a good approximation for the d- but not for the s-electrons. On the other hand it is well known that the s-electron contribution is non-negligible [23]. So we include the s-electrons in pseudopotential perturbation theory and account for s-d hybridization by setting the numbers N_s and N_d of s- and d-electrons equal to the values resulting from a selfconsistent band-structure calculation for the crystalline metal [24]. The s-electron pseudopotential is modelled by an empty-core potential with core radius R_c fitted to the structure of liquid metals. Screening is treated in Ichimaru – Utsumi [25] approximation to the dielectric function of the electron gas. This yields the following expression for the total pair potential

$$\Phi(R_{ij}) = \Phi_s(R_{ij}) + \Phi_{d,rep}(R_{ij}) + \Phi_{d,bond}(R_{ij}) \quad . \qquad (10)$$

Table I of Ref. 21 contains all necessary input-parameters for the calculation of the interatomic forces.

One of the main advantages of the bond order concept is the readily generalization to $A_x B_{1-x}$ alloys. For the reference system we have chosen a Bethe-lattice with a coordination number $Z = 12$ and a random occupation of all sites. The generalization of eqns. 8 and 9 yields [21]

$$G_{ii}^\alpha(E) = \frac{1}{E - E_{d,i}^\alpha - \Delta_i^\alpha} \qquad \alpha = A, B \qquad (11.a)$$

$$\Delta_i^\alpha(E) = Zh_{\alpha\alpha}(x_\alpha S_{\alpha\alpha} + x_\beta S_{\beta\beta}) \qquad \alpha = A, B \quad \alpha \neq \beta \qquad (11.b)$$

$$G_{ij}^{\alpha\beta}(E) = S_{\alpha\beta}G_{ii}^\beta(E) \qquad \alpha, \beta = A, B \qquad (11.c)$$

where i, j are nearest-neighbour sites, and

$$S_{\alpha\alpha} = \frac{h_{\alpha\alpha}}{E - E_{d,i}^\alpha - (Z-1)h_{\alpha\alpha}(x_\alpha S_{\alpha\alpha} + x_\beta S_{\beta\beta})}) \qquad (12.a)$$

$$S_{\alpha\beta} = \frac{h_{\alpha\alpha}}{h_{\alpha\beta}} S_{\alpha\alpha} \qquad \alpha, \beta = A, B \quad . \qquad (12.b)$$

with $h_{AB} = \sqrt{h_{AA}h_{BB}}$. This completely determines the bond order potentials $\Phi_{\alpha\beta,bond}(R_{ij}) = h_{\alpha\beta}(R_{ij})\Theta_{ij}$. For the repulsive d-potential $\Phi_{\alpha\beta,rep}$ a straightforward generalization of the Wills – Harrison expression is taken [14] and the s-electron contribution $\Phi_{\alpha\beta,s}$ is given by the well known standard pseudopotential formulae [9].

Atomic and electronic structure

We have performed microcanonical molecular dynamics (MD) simulations for N = 1372 particles and a time increment of $\Delta t = 10^{-15}$ s. Around the nearest neighbour distance the pair interaction has an equilibrium between attractive d- and repulsive s-forces. At the scale of thermal energies ($\Phi - \Phi_{min} \simeq k_B T_M$, T_M is the melting temperature) the slope of the pair potential is softer than for simple metals. The MD simulations describe the liquid structure of pure transition-metals very well [26].

As an example for a glassy alloy we present th MD-results of amorphous $Ni_{35}Zr_{65}$. The electronic DOS illustrated in Fig. 1(a), shows a relatively narrow, nearly completely filled Ni d-band overlapping with a broad Zr d-band. From the imaginary part of the off-diagonal Green's function (Fig. 1(b)) we find that the Zr-Zr and Ni-Zr interactions are dominated by bonding combinations of nearest-neighbour d-states, leading to large bond orders $\Theta_{ZrZr} = -2.11$ and $\Theta_{Ni-Zr} = -1.97$, whereas a nearly complete cancellation between bonding and antibonding interactions leads to a small $\Theta_{NiNi} = -0.59$. This explains the strong non-additivity of the pair interactions (see

Fig. 1(c)). The results of the MD-quench ($\frac{dT}{dt} \simeq 10^{14}$ Ks^{-1}) are shown together with the results of neutron-scattering experiments with isotopic substitution [27] in Fig. 2. We note that for all significant features we find a full agreement between theory and experiment especially in the pronounced chemical short-range order (CSRO). The form of the partial G_{IJ}'s is far away from that of a random packing model and points to a topological SRO as well. $Ni_{35}Zr_{65}$ crystallizes in the $CuAl_2$ structure and the peaks in the reduced radial distribution functions show a reasonable correlation with the interatomic distances in the crystal (see also Table 1).This correspondence between the crystalline and amorphous phases is also valid for other Ni-based glasses like $Ni_{33}Y_{67}$, Ni_xZr_{1-x} (x = 0.35, 0.50, 0.65) and Ni_xNb_{1-x} (x = 0.44, 0.62) [22]. For instance the study of the Ni-Ni-Ni bond-angle distribution (Fig. 3) shows a clear trend from trigonal-prismatic ($Ni_{33}Y_{67}$, $Ni_{35}Zr_{65}$) to a polytetrahedral ($Ni_{44}Nb_{56}$) local order in the glass as in the crystal. This is also confirmed in the variations of the Ni-Ni correlation functions (Fig. 4(a)). In Ni-Y glasses the position of the first three peaks in $g_{NiNi}(R)$ corresponds almost exactly to the peaks in the B-B correlation function in $Ni_{64}B_{36}$ and $Ni_{81}B_{19}$ [28], in the Ni-Nb glasses the form of $g_{NiNi}(R)$ is much closer to the dense-random-packing of hard spheres (DRPHS) limit. The same trend is observed in Ni_xZr_{1-x} glasses with increasing Ni-content (Fig. 4(b)). The origin of these trends can now be traced back to the variations of the interatomic forces and of the electronic structure.
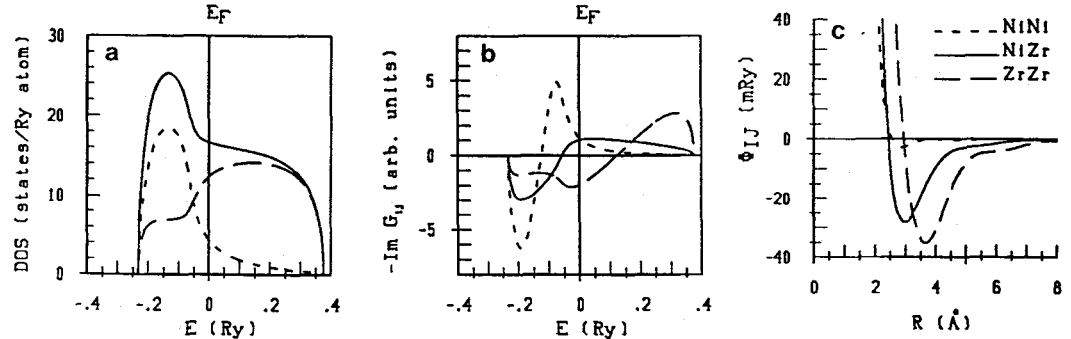

Figure 1: (a,b) Electronic DOS n(E) and imaginary part of the off-diagonal Green's function $G_{ij}(E)$ for a random Bethe-lattice for $Ni_{35}Zr_{65}$. (c) Effective interatomic potentials $\Phi_{IJ}(R)$ for $Ni_{35}Zr_{65}$.
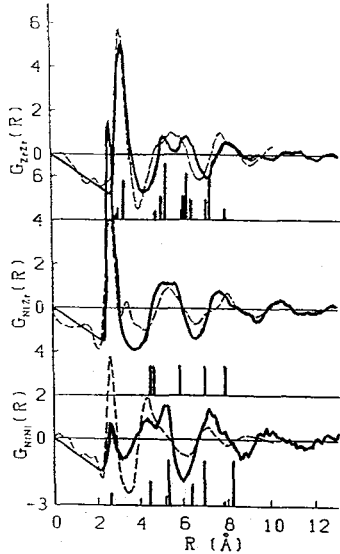

Figure 2: Partial reduced radial distribution functions $G_{IJ}(R)$ for amorphous $Ni_{35}Zr_{65}$. Full lines – theory, dashed lines – experiment (after Ref. 27). The vertical bars represents the interatomic distances in the $CuAl_2$-type compound $NiZr_2$ and they are scaled to the number of neighbours.

Table 1: Interatomic distances d and coordination numbers N_{IJ} in $Ni_{35}Zr_{65}$ glass and the related intermetallic compound $NiZr_2$, experimental data from Ref. 27.

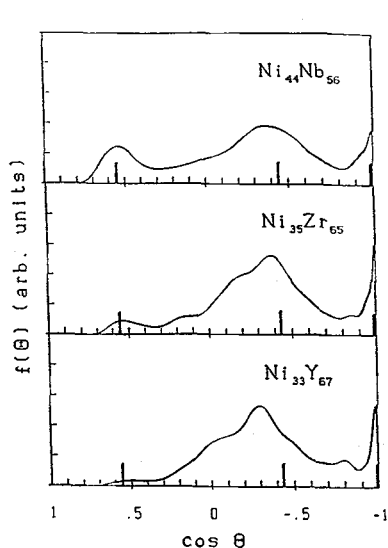| | $Ni_{35}Zr_{65}$-Glass | | | | $NiZr_2$-Crystal | |
| | d(Å) | N_{IJ} | d(Å) | N_{IJ} | d(Å) | N_{IJ} |
	Theory		Experiment			
Ni-Ni	2.60	1.2	2.45	3.3	2.63	2
Ni-Zr	2.70	8.2	2.85	8.6	2.76	8
Zr-Ni	2.70	4.4	2.85	4.8	2.76	4
Zr-Zr	3.25	10.7	3.30	11.0	2.99-3.43	11

Figure 3: Ni-Ni-Ni bond-angle distribution in Ni-TM glasses. The bond-angle in the Ni-chains of the NiZr crystal and in a regular icosahedron are indicated.
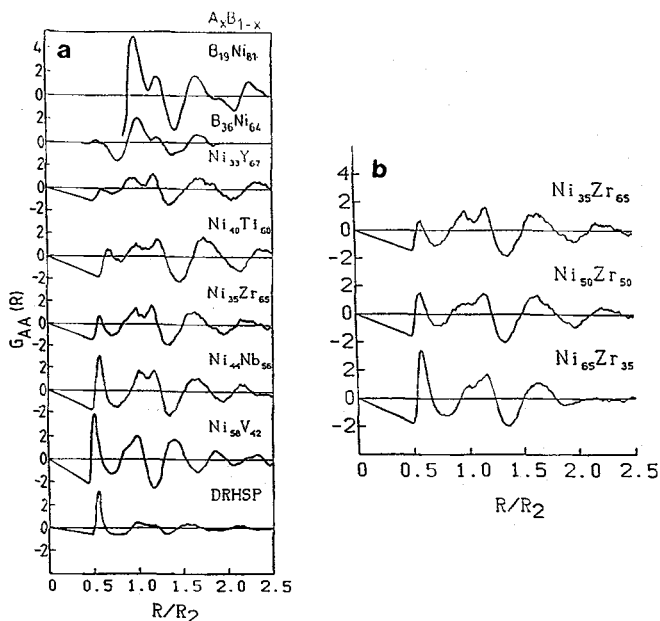

Figure 4: (a,b) Ni-Ni and B-B correlation functions in Ni-B and Ni-TM glasses. Distances are scaled to the position of the second peak.
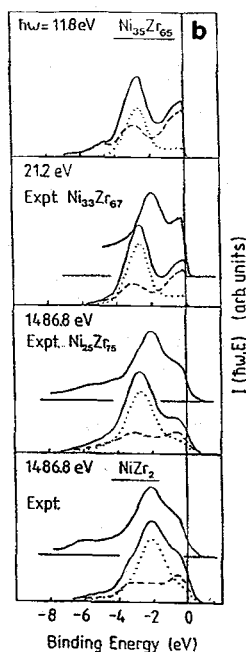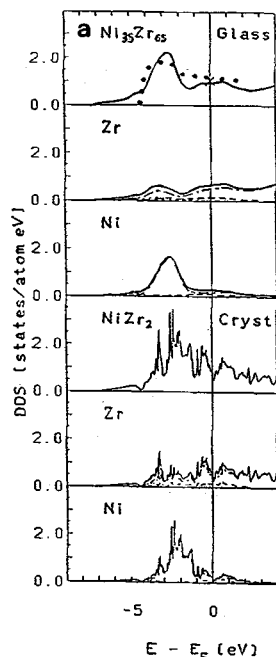

Figure 5: (a) Total, site- and angular-momentum decomposed electronic DOS for crystalline and glassy $Ni_{35}Zr_{65}$. Full line: total and local DOS, dotted line: partial DOS of s-states, dashed line: p-states, dot-dased line: d-staes. The full dots mark the d-DOS on a Bethe-lattice.(b) Calculated and measured photoemission intensities $I(E,\hbar\omega)$at different exciting energies. Full line: total intensity, dotted line: Ni-contribution, dashed line: Zr-contribution. The experimental results are from Refs. 29 and 30.

The computer generated structural models may serve as the basis for a selfconsistent supercell calculation of the electronic structure and photoemission intensities [15,16]. As in the atomic structure we find a strong correlation between the crystalline and amorphous (liquid) phases (Fig. 5). The calculated DOS agrees reasonably well with the Bethe-lattice results and shows the consistency of our theory.

Concluding we have presented a novel hybridized NFE-TBB approach to interatomic forces in disordered transition-metal alloys. This allows to investigate the structural and electronic properties of transition-metal glasses at a level of detail previously not possible. Ongoing work in our group extends thes investigations to Fe- and Co-based alloys and p-d systems.

Acknowledgements

References

[1] D. Turnbull and M. H. Cohen, J. Chem. Phys. 34, 120 (1961).

[2] N. E. Cusack, *The Physics of Structurally Disordered Materials*, (Hilger, Bristol 1987).

[3] J. Hafner, in *Glassy Metals I*, ed. by H. J. Güntherodt and H. Beck (Springer, Berlin 1981), p. 93.

[4] S. P. Elliot, *Physics of Amorphous Materials*, (Longmans, London 1989).

[5] P. R. Nelson and F. Spaepen, in *Solid State Physics*, ed. by H. Ehrenreich and D. Turnbull (Academic, New York 1989), vol. 42, p. 1.

[6] F. H. Stillinger and T. A. Weber, Phys. Rev. 31, 1954 (1985); ibid. p. 5262.

[7] J. Hafner, J. Phys. F18, 153 (1988).

[8] V. Heine and D. Weaire, in *Solid State Physics*, ed. by H. Ehrenreich and D. Turnbull (Academic, New York 1989), vol. 24, p. 247.

[9] J. Hafner, *From Hamiltonians to Phase Diagrams*, (Springer, Berlin 1987).

[10] P. H. Gaskell, in *Glassy Metals II*, ed. by H. Beck and H. J. Güntherodt, (Springer, Berlin 1983), p. 5.

[11] *Many-Atom Interactions in Solids*, ed. by R. M. Nieminen, M. J. Puska, and M. J. Manninen (Springer, Berlin 1990), p. 34, p. 48, p.158.

[12] D. G. Pettifor, in Ref. 11 p. 64.

[13] M. W. Finnis and J. E. Sinclair, Phil. Mag. A50, 45 (1984).

[14] J. H. Wills and W. A. Harrison, Phys. Rev. B28, 4364 (1983)

[15] W. Jank, Ch. Hausleitner, and J. Hafner, J. Phys. Condens. Matter 3, 4477 (1991).

[16] W. Jank, Ch. Hausleitner, and J. Hafner, Europhys. Lett., in print (1991)

[17] A. P. Sutton, M. W. Finnis, D. G. Pettifor, and Y. Ohta, J. Phys. C21, 35 (1988).

[18] D. G. Pettifor, Comm. Phys. 1, 141 (1977).

[19] O. K. Andersen and A. R. Mackintosh, in *Electrons at the Fermi surface*, ed. by M. Springford, Chap. 5.3 (Cambridge Univ. Press, 1980).

[20] E. N. Economou, *Green's Functions in Quantum Physics*, (Springer, Berlin 1979), p. 232.

[21] Ch. Hausleitner and J. Hafner, Phys. Rev. B44, I + II in print (1991).

[22] O. K. Andersen and O. Jepsen, Physica B91, 317 (1977).

[23] D. G. Pettifor, in *Physical Metallurgy*, ed. by P. Haasen and R. W. Cahn, (North-Holland, Amsterdam 1983), vol. 1, chap. 3.

[24] V. L. Moruzzi, *Thesis* (Technical University Vienna), unpublished.

[25] S. Ichimaru and K. Utsumi, Phys. Rev. B24, 7385 (1981).

[26] Ch. Hausleitner, G. Kahl, and J. Hafner, J. Phys. Condens. Matter 3, 1589 (1991).

[27] T. Mizoguchi, S. Yoda, N. Akutsu, S. Yamada, J. Nishioka, T. Suemasa, and N. Watanabe, in *Rapidly Quenched Metals*, ed. by S. Steeb and H. Warlimont (Elsevier, New York 1985), p. 483.

[28] S. Steeb and P. Lamparter, J. Non-Cryst. Solids 61+62, 237 (1984).

[29] A. Amamou, Solid State Comm. 33, 1019 (1980).

[30] P. Oelhafen, in Ref. 10, p.283 and in *Liquid and Amorphous Materials*, ed. by E. Lüscher, G. Fritsch, and G. Jacucci (Martinus Nijhoft, Dordrecht 1987), p. 333.