

Electronic theory of the chemical short-range order in liquid and amorphous transition-metal alloys

A. Pasturel* and J. Hafner

Institut für Theoretische Physik, Technische Universität, Wien, Karlsplatz 13, A-1040 Wien, Austria

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We present microscopic calculations of the chemical short-range order in amorphous and liquid alloys of two transition metals. Our approach is based on a model one-band tight-binding Hamiltonian and a thermodynamic variational technique founded on the Gibbs-Bogolyubov inequality and a hard-sphere Yukawa fluid as a reference system. We calculate the Bhatia-Thornton partial structure factors of $\text{Ni}_x\text{Ti}_{1-x}$ and $\text{Ni}_x\text{Zr}_{1-x}$ alloys and find good agreement with experiment.

I. INTRODUCTION

Recently several accurate experimental determinations of the three partial structure factors of amorphous transition metal alloys have been reported. The results for $\text{Ni}_{40}\text{Ti}_{60}$,¹ and $\text{Ni}_x\text{Zr}_{1-x}$ ($x=0.35, 0.50, 0.65$),^{2,3} as well as for $\text{Ni}_{35}\text{Y}_{65}$,⁴ have shown a degree of chemical ordering which can vary either with the composition as in the case of the $\text{Ni}_x\text{Zr}_{1-x}$ system or with the partner species as in the $\text{Ni}_x\text{M}_{1-x}$ series ($M=\text{Ti}, \text{Zr}, \text{Y}$). If experimentally it is difficult to bring the chemical short-range order (CSRO) to light, a microscopic theory of the CSRO seems an even harder task.

In principle this goal could be achieved in two different ways: (a) Given the interatomic forces, computer simulations are used to calculate the structure of the glass. However, reliable interatomic forces may only be derived from pseudopotential theory for simple metals and their alloys;^{5,6} for transition metals only empirical potentials of questionable validity are available. (b) Given an expression for the free energy as a function of the atomic coordinates, the equilibrium configuration is obtained by minimization of the free energy. As total energies are easily calculated in a tight-binding approximation, this approach appears to be attractive for transition metals as well.

A straightforward minimization of the free energy with respect to the atomic coordinates is, of course, out of the question—even for moderately large clusters of atoms. On the other hand, we might parametrize the structure in a simple way and minimize the free energy with respect to a small number of relevant parameters. This is precisely what is done in a thermodynamic perturbation theory of the liquid state.

The simplest form of a thermodynamic perturbation theory is the variational approach based on the Gibbs-Bogolyubov inequality.⁷ According to this inequality, the exact free energy F of a system is always smaller than or equal to the free energy F_0 of a reference system plus the expectation value of the perturbation evaluated with the distribution functions of the reference system, i.e.,

$$F \leq F_0 + \langle H - H_0 \rangle_0, \quad (1.1)$$

H being the “exact” Hamiltonian of the metal or the alloy and H_0 that of the reference system.

The success of the variational method depends on the availability of an appropriate reference system; it is clear that the interesting properties of amorphous or liquid alloys with strong chemical interactions are beyond the grasp of hard-sphere models. However, with a more judicious choice of a reference system some progress might be achieved. Copestake *et al.*^{8–10} have shown that a mixture of hard spheres all having the same diameter but different charges and interacting through a screened Coulomb (Yukawa) potential is a good model for describing the structural manifestations of ordering in liquid alloys. Their idea was taken up by Hafner *et al.*^{11,12} who demonstrated that, combined with a very simple treatment of the electronic contributions to the free energy, the thermodynamic and structural properties of Li- and Na-based alloys may be calculated with good success. This has led the authors¹³ to use the thermodynamic variational treatment combined with pseudopotential-derived pair and volume forces and to provide the first microscopic theory of CSRO in simple-metal alloys.

The purpose of the present paper is to show how this approach can be extended to describe CSRO in liquid and amorphous transition-metal alloys. Of course the thermodynamic variational approach is strictly applicable only to liquid systems (where experimental information on the CSRO is extremely scarce)—for the amorphous alloys we will have to assume that their CSRO is essentially identical to that of a supercooled liquid alloy just above the glass-transition temperature. The thermodynamic variational technique is particularly interesting in this context because it requires only the knowledge of the total energy and is not restricted to pair-potential Hamiltonians. Indeed a tight-binding d -electron Hamiltonian is more appropriate for transition metals, many methods for calculating the electronic density of states are based on a tight-binding scheme.^{14–20} However, only a few of them include both the effects of short-range order and of charge

transfer; charge transfer is important because the degree of CSRO affects both the amount of charge transferred and its effect on the self-consistent one-electron potential of the alloy. Therefore, we have chosen to work with a tight-binding Cayley-tree method introduced by Falicov and co-workers.¹⁹

In Sec. II we recapitulate briefly the Bethe-lattice approximation used to calculate the self-consistent electronic density of states and the electronic ground-state energy of the alloy. The properties of the reference system are summarized in Sec. III. We present an application of this new variant of the variational technique to Ni₄₀Ti₆₀ and Ni_xZr_{1-x} ($x=0.35,0.50,0.65$) alloys in Sec. IV. We find that in Ni-Zr the CSRO varies strongly with composition, the comparison of the results obtained for Ni-Ti and Ni-Zr suggests that the CSRO depends on the difference ΔE_d of the atomic energy levels and on the band filling. We focus our attention on the structural properties and we demonstrate that we are able to reproduce the experimentally known neutron scattering data with good accuracy.

II. THE TIGHT-BINDING BOND MODEL

In general the total energy can be written as the sum of two terms, namely,

$$E_T = E_{\text{rep}} + E_{\text{bond}}, \quad (2.1)$$

where the labels imply that the division has been made in such a way that around the equilibrium volume the first contribution is repulsive and the second attractive (bonding). In a tight-binding model²⁰ it is generally assumed that the repulsive energy is well described by an empirical pair potential $\phi_{ij}(R)$ ($i, j = A, B$ is used to label the atomic species)

$$E_{\text{rep}} = \frac{1}{N} \sum_{\substack{\mu, \nu \\ \mu < \nu}} \phi_{ij}(R_{\mu\nu}), \quad (2.2)$$

whereas the attractive contribution stems from the quantum-mechanical bonding between the atoms. Within the tight-binding approximation this term is given by

$$E_{\text{bond}} = \int_{-\infty}^{E_F} N(E)E dE - E_{\text{el-el}} + E_{\text{ion-ion}}, \quad (2.3)$$

where $N(E)$ is the electronic density of states and E_F the Fermi energy. The first term represents the sum of the one-electron energies, the second the double-counting correction for the electron-electron interaction which has been counted twice in the first term. The third term stands for the interionic Coulomb interactions.

In this paper the electrons are described by a very simple one-band Hamiltonian

$$H_{\text{el}} = \sum_{\mu} \epsilon_{\mu} |\mu\rangle \langle \mu| + \sum_{\substack{\nu, \mu \\ \nu \neq \mu}} t_{\mu\nu} |\mu\rangle \langle \nu|, \quad (2.4)$$

where $|\mu\rangle$ represents a Wannier-type state on site μ for a given spin. The hopping integral $t_{\mu\nu}$ allows for electronic transitions between sites μ and ν . In an $A_x B_{1-x}$ alloy the atomic energy levels ϵ_{μ} assume one of two possible values ϵ_A and ϵ_B , depending on the random occupation of the

site μ by an atom of type A or B . The hopping integrals $t_{\mu\nu}$ can take three possible values t_{AA} , t_{AB} , or t_{BB} according to the occupation of the sites μ and ν .

Note that by using a one-band Hamiltonian we are treating all d orbitals as degenerate and neglect their directional properties—thus we are considering only the spherically averaged part of the d bonds. This is also the basis of Friedel's classical model for transition metals²⁰ and of Pettifor's²¹ recent theory for the heat of formation of transition metal alloys. Moreover, it is consistent with our structural model which considers only spherically averaged pair correlations.

For d -band metals experience suggests a pair interaction of the form $\phi_{ij}(R) = C_{ij}/R^m$ with $m = 8-10$,²¹ but little is known about the exact values of the exponent and of the prefactors. In our work we choose to circumvent these uncertainties in the following way.

We assume that the density of the alloy is well described by Végard's law. For the pure metals the hard-sphere diameter σ is determined by fitting the excess entropy of the liquid, respectively, supercooled liquid for the alloy, a mean hard-sphere diameter is calculated assuming that the total hard-sphere volume does not change on alloying. Furthermore we shall assume that E_{rep} is independent of the degree of CSRO (this appears to be a reasonable assumption because the interionic Coulomb interactions, which are affected by CSRO and charge transfer, have been absorbed in E_{bond}). With these simplifying assumptions, we can determine the equilibrium CSRO at a given density by varying E_{bond} with respect to the remaining parameters of the reference system.

A. The electronic density of states in the alloy

The electronic density of states $N(E)$ is given in terms of the configurationally averaged Green's function $\langle G_{\mu\mu} \rangle$ by

$$N(E) = -\frac{1}{\pi} \lim_{\delta \rightarrow 0} [\text{Im} \langle G_{\mu\mu}(E + \delta) \rangle]. \quad (2.5)$$

We use a tight-binding Green's-function technique analogous to the alloy Bethe-lattice method introduced by Brouers *et al.*²² and applied by Falicov and co-workers¹⁹ to describe short-range order in crystalline alloys. Other applications concern liquid s -band alloys like Cs-Au (Refs. 23 and 24) and crystalline alloys of transition metals^{25,26} and of simple metals.²⁷ We refer to these papers for a detailed description of the method, only the basic equations are summarized below.

In a crystalline alloy, the configurational average can be calculated in terms of the three parameters that characterize the atomic structure of the alloy: composition x , total coordination number Z , and chemical short-range order parameter α . In terms of Z and α the partial coordination numbers Z_{ij} are given by $Z_{ii} = Z(x_i + x_j\alpha)$ and $Z_{ij} = Zx_j(1 - \alpha)$, $i, j = A, B$. With these definitions, the Cayley-tree approximation leads to the following set of equations for the configurationally averaged Green's function $\langle G_{\mu\mu} \rangle$:²²

$$\langle G_{\mu\mu} \rangle = x_A G^A + x_B G^B, \quad (2.6)$$

$$G^i = (z - \epsilon_i - \Delta_i)^{-1}, \quad i = A, B, \quad (2.7)$$

with the self-energies Δ_i determined by the solutions of

$$\Delta_i = Z_{ii} t_{ii}^2 / (z - \varepsilon_i - \tilde{\Delta}_i) + Z_{ij} t_{ij}^2 / (z - \varepsilon_j - \tilde{\Delta}_j), \quad (2.8)$$

$$\tilde{\Delta}_i = \Delta_i (Z - 1) / Z. \quad (2.9)$$

The quantities that describe the atomic structure of a liquid alloy are the partial pair correlation functions $g_{ij}(r)$ measuring the probability to find an (ij) pair at a distance r . Following Movaghar and Schirmacher²⁸ we generalize (2.8) by replacing $Z_{ij} t_{ij}^2$ by $\rho \int g_{ij}(r) t_{ij}^2(r) d^3r$, ρ being the number density. The partial coordination number would then be given by $Z_{ij} = 4\pi\rho \int_0^{R_{\max}} g_{ij}(r) r^2 dr$ with a yet undetermined cutoff radius R_{\max} . Movaghar and Schirmacher²⁸ propose to avoid the uncertainty connected with a choice of R_{\max} by letting it go to infinity: Now electronic transitions to any site in the system are allowed (for a deeper discussion of configurational averages on Z -fold coordinated Cayley trees we must refer to their paper). Formally this corresponds to $Z \rightarrow \infty$ and makes a distinction between Δ_i and $\tilde{\Delta}_i$ unnecessary so that the self-energies are now the solutions of the equations

$$\Delta_A = \frac{\rho x_A \int t_{AA}^2(r) g_{AA}(r) d^3r}{z - \varepsilon_A - \Delta_A} + \frac{\rho x_B \int t_{AB}^2(r) g_{AB}(r) d^3r}{z - \varepsilon_B - \Delta_B}, \quad (2.10a)$$

$$\Delta_B = \frac{\rho x_B \int t_{BB}^2(r) g_{BB}(r) d^3r}{z - \varepsilon_B - \Delta_B} + \frac{\rho x_A \int t_{AB}^2(r) g_{AB}(r) d^3r}{z - \varepsilon_A - \Delta_A}. \quad (2.10b)$$

The distance dependence of the d - d hopping integrals is usually assumed to follow a

$$t_{ij}(r) = t_{ij}^0 (r_0/r)^5 \quad (2.11a)$$

or a

$$t_{ij}(r) = t_{ij}^0 \exp(-3\Delta r/r_0), \quad \Delta r = r - r_0 \quad (2.11b)$$

law.²⁹ In both cases r_0 is a mean nearest-neighbor distance, $t_{ij}^0 = t_{ij}(r_0)$. The prefactor 3 in the exponent of (2.11b) is determined by general experience—in our case only the integral over the square of the hopping integral multiplied with the correlation function enters the calculation. Because of the rapid decay of $t_{ij}(r)$ and of the relative sharpness of the first peak in the correlation functions (typically the width at half maximum is about 15% of the nearest-neighbor distance) the precise form of the variation of t_{ij} with distance is of little importance, we have adopted the form (2.11b).

B. The charge transfer

The Fermi energy in the alloy is determined by the charge conservation condition

$$\begin{aligned} x_A n_A^0 + x_B n_B^0 &= \int_{-\infty}^{E_F} N(E) dE \\ &= \int_{-\infty}^{E_F} [x_A N_A(E) + x_B N_B(E)] dE, \end{aligned} \quad (2.12)$$

where n_i^0 denotes the number of valence electrons in the pure metal i and $N_i(E)$ is the partial density of states at the i sites in the alloy. The charge transfer is then given by

$$\delta n_i = n_i - n_i^0, \quad (2.13)$$

with

$$n_i = \int_{-\infty}^{E_F} N_i(E) dE, \quad i = A, B. \quad (2.14)$$

A change of the number of valence electrons at a given site i will shift the energy levels at that site. To calculate this shift $\Delta\varepsilon_i$, we have to specify the electron-electron interactions. Following Holzhey *et al.*³⁰ and Giner *et al.*³¹ we adopt an interpolation formula

$$V(r) = e^2 / (r + U^{-1}e^2), \quad (2.15)$$

which smoothly interpolates between a Hubbard-type model for the intraatomic interactions and a Coulomb potential for the interatomic interactions at long distances. With this form of the electron-electron interactions, the shift of the atomic energy levels is given by³⁰

$$\Delta\varepsilon_A = U \delta n_A + x_A \rho \delta n_A \int [g_{AA}(r) - g_{AB}(r)] V(r) d^3r, \quad (2.16a)$$

$$\Delta\varepsilon_B = U \delta n_B + x_B \rho \delta n_B \int [g_{BB}(r) - g_{AB}(r)] V(r) d^3r. \quad (2.16b)$$

Note that Eqs. (2.6)–(2.16) have to be solved self-consistently: Starting from the pure metal values of the ε_i , the valence charges on both constituents are calculated according to (2.13), this charge transfer changes the ε_i according to (2.16) and the operation has to be repeated until self-consistency has been achieved.

C. The total energy

If we drop E_{rep} (because it remains constant when the CSRO varies), the relevant part of the total energy is just given by the bond energy (2.3). As in (2.15) and (2.16) we split the electron-electron interaction energy $E_{\text{el-el}}$ into an intraatomic and an interatomic term and combine the latter with the interionic interactions

$$-E_{\text{el-el}} + E_{\text{ion-ion}} = -E_{\text{el-el}}^{\text{intra}} + (E_{\text{ion-ion}} - E_{\text{el-el}}^{\text{inter}}). \quad (2.17)$$

In accordance with our model for the electron-electron interactions, the total intraatomic electron-electron energy is written as

$$E_{\text{el-el}}^{\text{intra}} = \frac{1}{2} x_A n_A^2 U + \frac{1}{2} x_B n_B^2 U \quad (2.18)$$

and the interatomic term as²⁴

$$\begin{aligned} E_{\text{ion-ion}} - E_{\text{el-el}}^{\text{inter}} &= -2\pi\rho \left[x_A^2 [2n_A \delta n_A + (\delta n_A^2)] \int_0^\infty g_{AA}(r) V(r) r^2 dr \right. \\ &\quad + 2x_A x_B (n_A \delta n_B + n_B \delta n_A + \delta n_A \delta n_B) \int_0^\infty g_{AB}(r) V(r) r^2 dr \\ &\quad \left. + x_B^2 [2n_B \delta n_B + (\delta n_B^2)] \int_0^\infty g_{BB}(r) V(r) r^2 dr \right]. \end{aligned} \quad (2.19)$$

Equations (2.3), (2.18), and (2.19) complete our expression for the ground-state energy of a given atomic configuration represented by a set of pair correlation functions $g_{ij}(r)$.

III. THE HARD-SPHERE YUKAWA (HSY) REFERENCE SYSTEM

Copstake *et al.*⁸⁻¹⁰ have shown that ordering phenomena in molten salts, liquid semiconductors, and even liquid metallic alloys may be modelled by a hard-sphere Yukawa fluid treated in the mean-spherical approximation (MSA). The MSA for a system of hard spheres of diameter σ and Yukawa tails is defined by the Ornstein-Zernike equations for the partial direct and total correlation functions $c_{ij}(r)$ and $h_{ij}(r)$ in conjunction with the MSA closure conditions ($\beta = 1/k_B T$)

$$c_{ij}(r) = -\beta\Phi_{ij} = -\beta Q_i Q_j \exp(-\kappa r)/r, \quad r > \sigma, \quad (3.1a)$$

$$h_{ij}(r) = -1, \quad r < \sigma. \quad (3.1b)$$

Here the Q_i are the charges carried by the hard spheres and κ is a screening constant. Waisman³² has shown that if the "charge neutrality condition"

$$x_A Q_A + x_B Q_B = 0 \quad (3.2)$$

is respected, the three coupled integral equations defining the $c_{ij}(r)$ decouple into two independent equations, one for the direct correlation function $c_{NN}(r)$ describing the number-density fluctuations and one for the correlation function $c_{cc}(r)$ describing the concentration fluctuations

[$c_{NN}(r)$, $c_{cc}(r)$, and $c_{Nc}(r)$ have been introduced by Bhatia and Thornton³³]; the cross term $c_{Nc}(r)$ coupling the number-density and concentration fluctuations is identically zero in this approximation. The resulting integral equation for $c_{NN}(r)$ is identical to the Percus-Yevick equation for a monoatomic hard-sphere system, so we know analytical solutions for the partial structure factors³⁴ and for the thermodynamic functions.^{35,36} The integral equation for $c_{cc}(r)$ has been solved analytically by Waisman.³² The result may be expressed in terms of a parameter w which is the solution of the quartic equation

$$\beta\epsilon\eta = \frac{w[Z - w/2 \exp(Z)]}{12\{1 + w[1 - \exp(-Z)]/2Z\}^4} \quad (3.3)$$

[η is the hard-sphere packing fraction,

$$\eta = \rho\pi\sigma^3/6, \quad Z = \kappa\sigma,$$

and

$$\epsilon = -x_A x_B (Q_A - Q_B)^2 \exp(-\kappa\sigma)/\sigma$$

is the strength of the ordering potential at hard contact]. The direct correlation function $c_{cc}(r)$ is then given by

$$c_{cc}(r) = \begin{cases} -\frac{\beta\epsilon w}{p} \frac{1 - \exp(-Zp)}{Z} + w \frac{\cosh(Zp) - 1}{2Z^2 \exp(Z)}, & p < 1 \\ \beta\epsilon \exp[-Z(p-1)]/p, & p > 1, \end{cases} \quad (3.4)$$

with $p = r/\sigma$.

The Fourier-transform $c_{cc}(q)$ of the direct correlation function is then given by

$$c_{cc}(q) = \frac{4\pi\beta\epsilon}{q} A_1 \left[\frac{1 - \cos(q\sigma)}{q} - \frac{q}{q^2 + \kappa^2} \right] + A_2 \left[\frac{\exp(-\kappa Z) [\kappa \sin(q\sigma) + q \cos(q\sigma)]}{q^2 + \kappa^2} \right] - A_3 \left[\frac{\kappa \sinh(Z) \sin(q\sigma) - q \cosh(Z) \cos(q\sigma)}{q^2 + \kappa^2} \right], \quad (3.5)$$

with

$$\begin{aligned} A_1 &= \frac{w}{\kappa} \{w/[2Z \exp(Z)] - 1\}, \\ A_2 &= \sigma \exp(Z) - w/\kappa, \\ A_3 &= w^2/[\kappa Z \exp(Z)]. \end{aligned} \quad (3.6)$$

The static structure factor is then simply

$$S_{cc}(q) = x_A x_B [1 - n c_{cc}(q)]^{-1}.$$

The analytical expression for c_{NN} (in real and in reciprocal space) and for S_{NN} are well known and need not to be repeated here. The partial pair correlation functions are given by

$$g_{cc}(r) = \frac{1}{2\pi^2 r \rho} \int_0^\infty \{[1 - \rho c_{cc}(q)]^{-1} - 1\} \sin(qr) q dq, \quad (3.7a)$$

$$g_{NN}(r) = \frac{1}{2\pi^2 r \rho} \int_0^\infty \{[1 - \rho c_{NN}(q)]^{-1} - 1\} \sin(qr) q dq, \quad (3.7b)$$

and are related to the $g_{AA}(r)$, $g_{AB}(r)$, and $g_{BB}(r)$ through

$$g_{AA}(r) = g_{NN}(r) + \frac{x_B}{x_A} g_{cc}(r), \quad (3.8a)$$

$$g_{BB}(r) = g_{NN}(r) + \frac{x_A}{x_B} g_{cc}(r), \quad (3.8b)$$

$$g_{AB}(r) = g_{NN}(r) - g_{cc}(r). \quad (3.8c)$$

Analytical expressions for the thermodynamic functions of this reference system may be derived using the coupling constant formalism with the final result for the free energy F (Ref. 13)

$$F_{\text{HSY}} = \frac{3}{2} k_B T + \Delta H_{\text{ord}} - T(S_{\text{HS}} + \Delta S_{\text{ord}}). \quad (3.9)$$

S_{HS} is the entropy of the hard-sphere system (we used the Carnahan-Starling expression³⁵) and

$$\Delta H_{\text{ord}} = -\epsilon w / 2 \quad (3.10a)$$

and

$$\Delta S_{\text{ord}} = \frac{[f(w) - f(0)]}{2\eta} \quad (3.10b)$$

are the contributions to the enthalpy and the entropy of formation associated with a nonvanishing ordering potential (i.e., with an $\epsilon \neq 0$). The function $f(w)$ is given by

$$f(w) = -\frac{B_1 + B_2 w + B_3 w^2}{72B_4^2(1 + B_4 w)^3}, \quad (3.11)$$

with

$$\begin{aligned} B_1 &= Z \{ 2 / [\exp(Z) - 1] - 1 \}, \\ B_2 &= -3[1 - 3 \exp(-Z)] / 2, \\ B_3 &= \exp(-Z)[1 - \exp(-Z)] / (4Z), \\ B_4 &= [1 - \exp(-Z)] / (2Z). \end{aligned} \quad (3.12)$$

Equation (3.3)–(3.12) contain the analytical description of the reference system needed in the variational calculation.

$$\begin{aligned} E_T(\beta\epsilon, \kappa) &= \int_{-\infty}^{E_F} EN(E; \beta\epsilon, \kappa) dE - \frac{1}{2} U [x_A n_A^2(\beta\epsilon, \kappa) + x_B n_B^2(\beta\epsilon, \kappa)] \\ &\quad - 2\pi\rho x_A x_B \{ 2[\delta n_B(\beta\epsilon, \kappa) - \delta n_A(\beta\epsilon, \kappa)][n_B(\beta\epsilon, \kappa) - n_A(\beta\epsilon, \kappa)] \\ &\quad + [\delta n_A(\beta\epsilon, \kappa) - \delta n_B(\beta\epsilon, \kappa)]^2 \} \int_0^\infty g_{cc}(r) V(r) r^2 dr. \end{aligned} \quad (4.2)$$

The density of states and the charge transfer depend on the degree of CSRO expressed by the coordinates $\beta\epsilon$ and κ , for each set of $(\beta\epsilon, \kappa)$ they have to be calculated self-consistently.

In principle the free energy would have to be minimized with respect to the full set of parameters $(\sigma, \beta\epsilon, \kappa)$ of the reference system. However, as explained in Sec. II, we choose to fix σ by fitting to the pure-metal entropies and to vary only the two parameters $\beta\epsilon$ and κ which enter that part of the free energy which is sensible to the CSRO. Now we find that this is consistent with our structural model: In our symmetric HSY model, size effects and CSRO are completely decoupled, we have $g_{Nc}(r) = 0$. Of course this limits the applicability of the method to systems where the size effect can be expected to be small: to replace the individual hard-sphere diameters by a mean atomic diameter is well justified for Ni-Ti, still acceptable for Ni-Zr, but not for Ni-Y. This simplification is also not unimportant in order to make the computational effort tractable: We have to minimize F with respect to two parameters, and each single $F(\beta\epsilon, \kappa)$ involves a self-consistent tight-binding calculation. To include a third parameter would mean to increase an already large computational effort by nearly 1 order of magnitude.

Our method is similar to earlier attempts³⁷ to calculate the CSRO in disordered systems which are also based on

IV. THERMODYNAMIC VARIATIONAL TECHNIQUE FOR CALCULATING THE CSRO IN LIQUID AND AMORPHOUS TRANSITION METAL ALLOYS

A. Variational expression for the free energy

With the ground-state energy E_T as a function of the correlation functions given by Eqs. (2.3), (2.18)–(2.19), and the reference system free energy and correlation functions expressed in terms of the parameters ϵ and κ of the HSY model in Eqs. (3.3)–(3.12), we can now give an explicit expression for the variational upper bound to the free energy

$$\begin{aligned} F &\leq F_{\text{HSY}} + \langle H - H_{\text{HSY}} \rangle_{\text{HSY}} \\ &= \frac{3}{2} k_B T + E_T(\beta\epsilon, \kappa) - TS_{\text{HSY}}(\beta\epsilon, \kappa). \end{aligned} \quad (4.1)$$

In the spirit of this inequality we will proceed to a minimization of the right-hand side of (4.1) with respect to the parameters $\beta\epsilon$ and κ which determine the strength of the ordering effects. For practical purposes the interatomic interactions are conveniently expressed in terms of the concentration-fluctuation correlation function:

the Bethe-lattice approximation and the HSY reference system. In that work however, the electronic and the atomic structure calculations were coupled together by equating the spectrally defined charge transfer and the electrostatic charges of the HSY system. We have two good reasons not to follow this convention: first, the definition of the charges in the HSY system is not unique (cf. the discussion in Ref. 13). Second, it is well known that a spectral definition of the charge transfer can yield quite misleading results. This method also excludes the conceivable solution of a charge transfer without chemical ordering. The variational method avoids all these problems.

B. Results

Before we discuss our results in detail we should make an attempt to justify the extension of the variational approach to amorphous alloys, i.e., to nonequilibrium systems. It is necessary to make the connection with experiment, since diffraction data on the liquid alloys are not available, but what can we really learn from such a comparison? From both diffraction experiments and computer simulations it is well known that the structure factors of a supercooled liquid just above the glass transition and of the glass of the same composition are very similar—the main characteristic difference being the shoulder in the

second peak of $S_{NN}(q)$, which is absent in the supercooled liquid. In our studies of amorphous and liquid simple metal alloys³⁸ we have compared the partial structure factors of glasses calculated with a molecular-dynamics quench technique with those derived using molecular dynamics and thermodynamic variational techniques (again with a HSY reference system) for the liquid and supercooled liquid states. Again we find that apart from the form of the second peak in $S_{NN}(q)$ the result of the variational calculation is in good agreement with the molecular-dynamics result and very similar to that of the glass. As far as the CSRO is concerned, the analogy between the supercooled liquid and the glass is even more pronounced. Thus it appears to be justified to compare the $S_{cc}(q)$ calculated for a supercooled liquid just above the glass transition temperature with the $S_{cc}(q)$ measured for the glass at room temperature. Details might still be different, but the comparison will certainly allow for a meaningful analysis of trends.

1. Ni-Ti

We begin by studying a system in which the assumption of a size ratio close to one should be reasonably well satisfied. The alloy selected is amorphous $\text{Ni}_{40}\text{Ti}_{60}$; for this system both neutron and x-ray diffraction experiments have been performed and the three partial Bhatia-Thornton structure factors have been resolved.¹ The experimental $S_{cc}(q)$ has significant oscillations over a wide range of momentum transfers with a main peak at $q=1.95 \text{ \AA}^{-1}$. $S_{Nc}(q)$ shows only very weak oscillations—this demonstrates that this system is indeed ideally suited for the HSY-variational calculation. The input parameters used for the calculation are shown in Table I. The values of ϵ_A and ϵ_B are taken from the tables of Herman and Skillman³⁹ assuming a $d^{n-1}s$ electronic configuration. In our model, the mean nearest-neighbor distance r_0 in (2.11) is set equal to σ ; the values t_{AA}^0 and t_{BB}^0 of the hopping integrals are deduced from the known bandwidth of the pure metals,⁴⁰ the t_{AB} hopping integral is set equal to the geometrical average of t_{AA} and t_{BB} , i.e., $t_{AB}=(t_{AA}t_{BB})^{1/2}$, which is a reasonable assumption for the alloys under consideration. The variational calculation was performed with a hard-sphere diameter σ fixed by assuming that a packing fraction of $\eta=0.56$ is representative of the alloy just above the glass-transition temperature. This is the value suggested by the extrapolated values of the excess entropies of the pure metals and the assumption that the total hard-sphere volume does not change on alloying. We find that within the uncertainty

TABLE I. Electronic parameters for $\text{Ni}_{40}\text{Ti}_{60}$ alloys. t_{ij}^0 and $\epsilon_{i(j)}^0$ are given in Ry. N_d is the number of d electrons.

	Ni	Ti
N_d	9	3
ϵ_d^0	-0.168	+0.168
t_{dd}^0	0.026	0.037

^aThe zero of the energy scale is chosen halfway between the atomic d levels of the constituents.

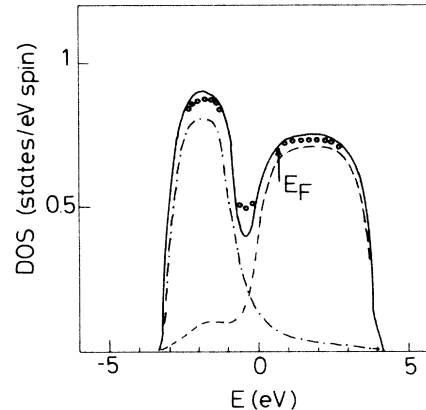


FIG. 1. Electronic density of states in amorphous $\text{Ni}_{40}\text{Ti}_{60}$. Solid line: including CSRO; circles: without CSRO, shown only where different; partial DOS of Ni (dashed-dotted) and Ti (dashed) sites.

of the experimental values and of an extrapolation over a rather large temperature interval, this value of the packing fraction fits the Ni-Ti and the Ni-Zr alloys at all concentrations. The result of the variational calculation at $T=700 \text{ K}$ is $\epsilon=-4.8 \text{ mRy}$ and $\kappa=2.3 \text{ a.u.}^{-1}$.⁴¹

The calculated electronic density of states shows the familiar shape for alloys of the early and late transition metals (see Fig. 1): Its spectrum is characterized by a binding energy shift and a splitting of the d band. The peak at high binding energies is related mainly to d states of the late transition metal (Ni) and the peak near E_F to those of the early transition metal (Ti) as can be seen from the partial densities of state shown in Fig. 1. The shift of the d states of the late transition metal results in a decrease of the local density of states (DOS) for Ni near E_F . In the ordered equilibrium configuration, the structure in the DOS is somewhat more pronounced than in a chemically random configuration. The narrowing of the subbands is a consequence of the fact that the CSRO tends to keep like atoms apart.

Figure 2 shows the partial structure factors $S_{NN}(q)$ and $S_{cc}(q)$ calculated with the variationally determined parameters. Our results compare very well with those determined in the neutron scattering experiment.¹ However, we should be fair enough to point out that only $S_{cc}(q)$ is a real prediction of the theory. $S_{NN}(q)$ is determined by the fitted packing fraction alone, so the agreement of the calculated $S_{NN}(q)$ with experiment merely confirms that our fitting procedure is reasonable. In some sense our calculation of the CSRO is the liquid-state analogue of the calculation of the short-range order parameters on a fixed mean lattice for a crystalline alloy. The amplitude of the first peak in $S_{cc}(q)$ depends on both ϵ and κ , i.e., on the strength and on the range of the ordering interaction. The position of the peak in $S_{cc}(q)$ at $Q_p \approx 0.58Q_1$ [where Q_1 is the position of the main peak in $S_{NN}(q)$] is very insensitive to the model parameters: It is almost independent of ϵ and tends to shift to slightly smaller values with decreasing κ .¹³ The good success of the variational calcula-

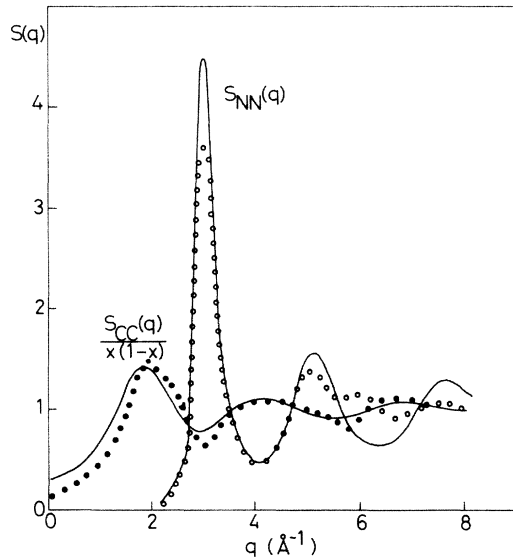


FIG. 2. Partial static structure factors $S_{NN}(q)$ and $S_{CC}(q)$ of amorphous $\text{Ni}_{40}\text{Ti}_{60}$. Solid line: variational calculation; open circles: experiment. $S_{Nc}(q)$ is identically zero in the reference system; this is well confirmed by the experiment, where the fluctuations in $S_{Nc}(q)$ never exceed ± 0.15 .

tion for $\text{Ni}_{40}\text{Ti}_{60}$ prompted us to extend our study to Ni-Zr alloys where we can in addition investigate the evolution of the CSRO as a function of composition.

2. Ni-Zr

Recently several structural investigations have been reported for this system. This provides an opportunity to study the CSRO as a function of composition. For $\text{Ni}_{35}\text{Zr}_{65}$ alloys, Lee *et al.*² determined the partial structure factors using neutron and x-ray diffraction combined with an isomorphous substitution technique. Mizoguchi *et al.*⁴² performed an isotope substitution experiment, but reported only the partial pair correlation functions for this alloy. For $\text{Ni}_{50}\text{Zr}_{50}$ and $\text{Ni}_{65}\text{Zr}_{35}$ the three partial structure factors were measured using the isotope substitution method by Fukunaga *et al.*³ and Lefebvre *et al.*,⁴³ respectively. It turns out that the CSRO is rather strong in the Ni-rich alloy ($\text{Ni}_{65}\text{Zr}_{35}$) and much weaker in the Zr-rich regime ($\text{Ni}_{35}\text{Zr}_{65}$); see Fig. 3(a) which shows the experimental $S_{cc}(q)$ for the three compositions. Our purpose is

TABLE II. Electronic parameters for $\text{Ni}_x\text{Zr}_{1-x}$ alloys. t_{ij}^0 and $\epsilon_{i(j)}^0$ are given in Ry. ϵ (in mRy) and κ (in a.u.⁻¹) are the optimal reference system parameters.

	Ni	Zr	
N_d	9	3	
ϵ_d^0	-0.162	0.162	
t_{dd}^0	0.026	0.053	
$\text{Ni}_{65}\text{Zr}_{35}$	$\text{Ni}_{50}\text{Zr}_{50}$	$\text{Ni}_{35}\text{Zr}_{65}$	
ϵ	-5.9	-4.2	-1.1
κ	1.1	2.3	2.6

to demonstrate that our model is able to explain this tendency.

The electronic input parameters used in our calculation are reported in Table II; as for the Ni-Ti alloy, the density of the alloy is interpolated linearly between the densities of the pure metals.⁴⁴ For all concentrations we performed the calculation at $T = 700$ K, this is within about 100 K from the glass temperatures.⁴⁵ Again we find that a packing fraction of $\eta = 0.56$ reproduces the extrapolated entropies reasonably well. The variationally determined ordering parameters ϵ and κ are also given in Table II; the

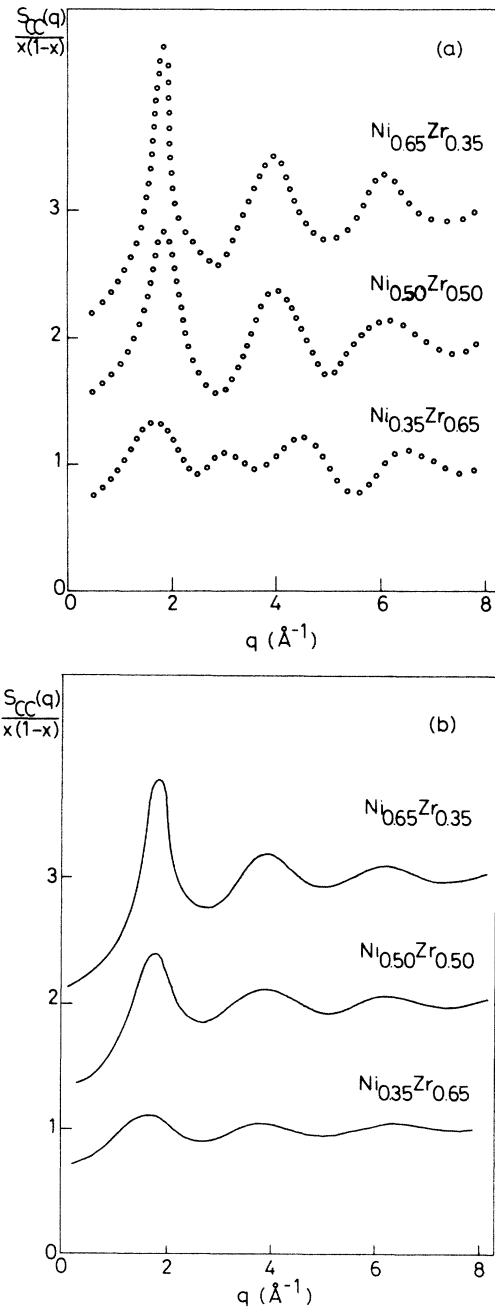


FIG. 3. (a) Experimental partial structure factors $S_{CC}(q)$ for several amorphous $\text{Ni}_x\text{Zr}_{1-x}$ alloys. (b) Calculated partial static structure factors $S_{CC}(q)$ for several amorphous $\text{Ni}_x\text{Zr}_{1-x}$ alloys.

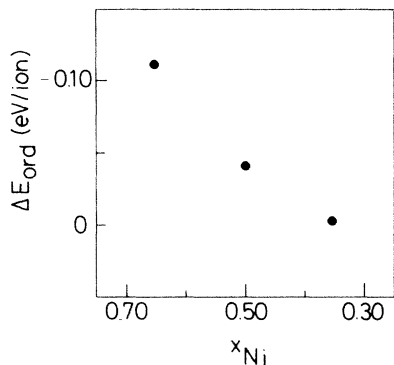


FIG. 4. Ordering energy of amorphous $\text{Ni}_x\text{Zr}_{1-x}$ alloys (ΔE_{ord} in eV).

theoretical $S_{cc}(q)$ for the three compositions are shown in Fig. 3(b). Keeping in mind that this is a calculation without any adjustable parameter relevant to the CSRO, the achieved agreement with experiment can certainly be considered as quite encouraging.

Next we look at the ordering energy; its variation with composition is shown in Fig. 4. Once more the ordering energy is maximum for the $\text{Ni}_{65}\text{Zr}_{35}$ alloy. The two main contributions to the ordering energies are the following:⁴⁶

$$\begin{aligned} \Delta E_{\text{ord}} &= E_T(\epsilon, \kappa) - E_T(0, 0) \\ &= \Delta E_{1e}(\epsilon, \kappa) + \Delta E_{\text{el-el}}(\epsilon, \kappa). \end{aligned} \quad (4.3)$$

The first contribution $\Delta E_{1e}(\epsilon, \kappa)$ is the variation of the one-electron energy [the first summand in Eqs. (2.3) or (4.2)] due to the modification of the electronic energy band upon ordering. This contribution may be positive or negative and depends essentially on the position of the Fermi level. The densities of state of the $\text{Ni}_x\text{Zr}_{1-x}$ alloys are displayed in Fig. 5. Like for other amorphous transition-metal alloys, the DOS's are characterized by the splitting and the shift of the d band. The effect of the CSRO is to increase the separation of the two d -band peaks. If the Fermi-level falls close to this pseudogap, the ordered state will be energetically more favorable because of the gain in band energy, but we have the opposite effect for a Fermi-energy which is not in this region. The $\text{Ni}_x\text{Zr}_{1-x}$ alloys represent an intermediate case with, however, an electronic configuration which is more favorable for CSRO in the Ni-rich alloy.

The second contribution comes from the intra-atomic electron-electron and the interatomic electron-electron and ion-ion interactions [see the second and third terms in Eqs. (2.3) and (4.2)] and their variation with the CSRO. The first term depends on the transferred charge, our calculation shows that electrons are transferred from Zr to Ni, and, as a result, the intra-atomic energy makes an attractive contribution to ΔE_{ord} , which is most pronounced for the $\text{Ni}_{65}\text{Zr}_{35}$ alloy. The variation of the second term with the degree of order depends on both the charge transfer and on the electronic difference between the two constituents and gives a repulsive contribution to ΔE_{ord} , which is again most important for the $\text{Ni}_{65}\text{Zr}_{35}$ alloy.

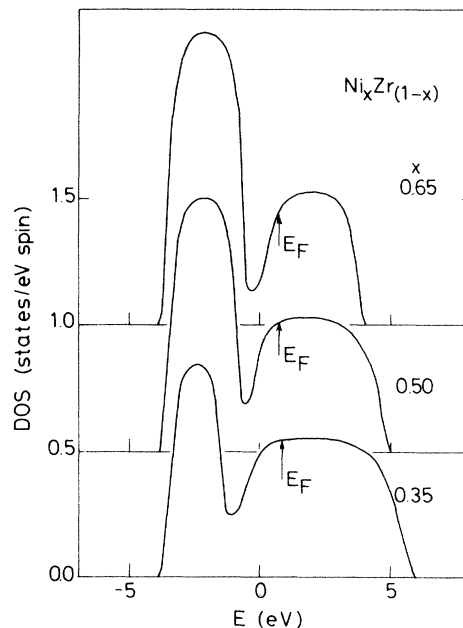


FIG. 5. Densities of states of amorphous $\text{Ni}_x\text{Zr}_{1-x}$ alloys.

Therefore, the ordering energy varies with both the charge transfer and the distortion of the band near the Fermi level. Its sign is determined by the competition between the mostly electrostatic electron-electron and ion-ion interaction effects and the effect of the d -band distortion. Both are very sensitive to the separation of the atomic energy levels of the alloy constituents and to the band filling and for a given composition, the ordering energy can be expressed as a function of these elemental electronic parameters. This result is very similar to that obtained by Gautier *et al.*,⁴⁷⁻⁴⁹ who described the ordering energy in binary fcc transition-metal alloys using a generalized perturbation expansion of the ground-state energy. A systematic study of the influence of these elemental parameters $[\epsilon_i, t_{ij}(R)]$ on the ordering energy and on the concentration-fluctuation structure factor $S_{cc}(q)$ is under way and will be presented elsewhere.

V. CONCLUSIONS

We have presented a very promising method for calculating the CSRO in amorphous and liquid alloys of transition metals. Our technique is based on a tight-binding d -electron Hamiltonian and a thermodynamic variational method. The optimal reference system may be determined by a free minimization of the upper bound to the exact free energy as a function of the open parameters of the reference system. As such it refers—at least in principle—to thermodynamic equilibrium configurations, but in agreement with earlier computer-simulation studies on simple metal alloys we find that calculations for the supercooled liquid phase yield useful information on the CSRO in the glassy phase.⁴⁶

First results for $\text{Ni}_{40}\text{Ti}_{60}$, $\text{Ni}_{65}\text{Zr}_{35}$, $\text{Ni}_{50}\text{Zr}_{50}$, and $\text{Ni}_{35}\text{Zr}_{65}$ alloys have been presented. The variationally determined concentration-fluctuation structure factors

compare very well with those determined from isotope substitution experiments on the amorphous alloys. The calculated electronic density of states shows the familiar splitting and shift of the *d* band, the calculated values of the DOS at the Fermi level are compatible with those inferred from experimental data.⁵⁰

Finally we think that the ordering potentials deduced in our calculations may serve as a basis for describing CSRO in more sophisticated and more realistic models of the atomic structure of transition-metal glasses.

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*Permanent address: Laboratoire de Thermodynamique et de Physico-Chimie Métallurgiques, Ecole Normale Supérieure d'Electrochimie et d'Electrometallurgie de Grenoble (ENSEEG), Domaine Universitaire, Boîte Postale No. 75, F-38402 Saint-Martin-d'Hères, France.

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