Structure Factors of Binary Aluminum-Nickel and Ternary Aluminum-Nickel-Silicon Liquid Alloys

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STRUCTURE FACTORS OF BINARY ALUMINUM-NICKEL AND TERNARY ALUMINUM-NICKEL-SILICON LIQUID ALLOYS

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A calculation of the structure of binary Al—Ni and of ternary Al—Ni—Si alloys based on a multicomponent hard sphere model and a square well like interatomic potential is developed in connection with chemical short range order in these alloys. Maret *et al.*[1] using the isotopic substitution method, measured the partial structure factors of the binary $Al_{80}Ni_{20}$ alloy. They obtained a prepeak in the partial Ni—Ni structure factor and a preminimum in the Ni—Al partial structure factor. We obtain the same features with a square well potential, but not with hard spheres. It has been shown by Chenal[2] that liquid ternary alloys at an amorphisable composition such as $Al_{65}Ni_{15}Si_{20}$ present a prepeak in the total structure factor, which is absent at a slightly different compostion of Ni: $Al_{75}Ni_5Si_{20}$. We show here that ternary hard sphere structure factors with additive hard spheres cannot explain any prepeak, while such a feature can be reproduced from square well attractions but only at the right composition.

1 INTRODUCTION

Research on metallic glasses considerably developed during the last decade due to the fundamental interests and possible applications (good mechanic or magnetic properties, resistance to corrosion...). Metallic glasses are generally complex multicomponent

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221

systems. Our purpose is to understand the structure of the corresponding alloy in the liquid state. Recently, Gazzillo et al.[3] analysed some experimental data of amorphous Ni—Ti alloys in terms of a non-additive hard sphere (NAHS) model. They showed that this model is able to account for the appearance of a prepeak in the diffraction pattern as a natural consequence of the set-up of a chemical short-range order (CSRO). Waisman[4] showed that for equal diameters of the two species of spheres, an analytical solution for the partial structure factors may be found. Hafner et al.[5,6] used the ordering potential $\varphi_{cc}(r)$ in the hard sphere Yukawa form and a mean pair potential $\varphi_{NN}(r)$ modeled by a hard sphere potential with a unique diameter (dependent on concentration). They calculated the partial static structure factors and the total diffraction intensity and showed that the thermodynamic 'anomalies' observed in these systems arise from the interplay of ordering effects induced by a preferred interaction between unlike atoms and packing effects. On the other hand, Pasturel et al.[7] presented a first principle study of CSRO in liquid (s,p) bonded alloys. Their approach is based on a optimized pseudopotential technique for the construction of the interatomic potentials and a thermodynamic variational technique based on the Gibbs-Bogoliubov inequality and hard sphere Yukawa reference potentials (for equal diameter case). Gopala Rao et al.[8] using the square well and the parameters of the pure metals analyzed the total structure factors of binary magnesium-zinc liquid alloys. They showed that a premaximum exists on the left hand side of the main peak and that it is not so pronounced than the experimental one.

We consider Al—Ni—Si since this alloy can be quenched in amorphous state over a large domain of concentrations. Chemical short range order is an important feature of the amorphous state which also persists in the liquid state at the same composition. For instance Maret et al.[1] showed that $Al_{80}Ni_{20}$ has an important CSRO while in $Al_{80}[Mn_x(FeCr)_{1-x}]_{20}$, the CSRO is less marked. With a n component alloy, it is difficult to study such trends from an ab initio theory of the interatomic potentials. We do not use the hard sphere Yukawa model for our ternary liquid alloys for different reasons: i) the analytical solution developed by Waisman is only applicable to alloys with equal diameters, in our case this approximation cannot be justified ii) even in this hypothesis the Yukawa potential cannot be easily extended to ternary alloys. We therefore consider an approach which can be straightforwardly extended to ternary systems, i.e. such as those used by Silbert and Young[9] for pure simple metals and by Gopala Rao et al.[10,11] for binary alloys. In such a model, potentials are simply based on hard spheres corrected by a repulsive ledge or by a square well interaction. Structure factors and correlation functions corresponding to a hard sphere potentials are obtained from the analytical expression of the PercusYevick (PY) approximation. Expressions for the pure and binary system are given in the literature[12,13]. For multicomponent systems, we used the expressions of the direct correlation function given by Hiroike[14] and Hoshino[15]. Structure factors corresponding to hard sphere potential plus a square well or repulsive ledge are calculated with the RPA method as used by Silbert and Young[9].

According to this approach it is interesting to look if CSRO and corresponding prepeak in the structure factor in liquid amorphisable alloys can be qualitatively explained on the basis of this simple model interaction.

2 PARTIAL STRUCTURE FACTORS OF N COMPONENT ALLOYS

2.1 Generalities

It can be shown[15] using Ornstein-Zernike equation that Ashcroft-Langreth's [A-L] partial structure factors can be written as:

$$S_{ij}(q) = \frac{|\tilde{I} - \tilde{C}(q)|_{ij}}{|\tilde{I} - \tilde{C}(q)|} \tag{1}$$

In this relation, $\tilde{I}$ means the identity matrix and $\tilde{C}(q)$ is a matrix which elements are:

$$\tilde{C}_{ij}(q) = \sqrt{\rho_i \rho_j} \int C_{ij}(r) \exp(i\vec{q}\vec{r}) d\vec{r} \tag{2}$$

where:

$C_{ij}(r)$ is the direct correlation function between i and j species.
ρ_i is the density number of the i-th species
$|\tilde{I} - \tilde{C}(q)|$ is the matrix determinant
$|\tilde{I} - \tilde{C}(q)|_{ij}$ is the cofactor of the determinant

An other definition of an other set of partial structure factors, often used in the literature, is due to Faber-Ziman[F-Z][16]:

$$a_{ij}(q) = 1 + \rho \int (g_{ij}(r) - 1) \exp(i\vec{q}\vec{r}) d\vec{r} \tag{3}$$

ρ is the total number density and $g_{ij}(r)$ the partial pair correlation functions. The relations between (AL) and (FZ) partial structure factors are given by:

$$S_{ij}(q) = \delta_{ij} + \sqrt{x_i x_j}(a_{ij}(q) - 1) \tag{4}$$

where x_j is the concentration of the jth component.

2.2 Direct correlation functions in the case of the hard sphere model

To calculate the partial structure factor $S_{ij}(q)$ from equation (2) we need to know the Fourier transform of the direct correlation function. For the n component hard sphere mixture, Hiroike[14] obtained the exact solution of the P-Y equation and gave the explicit forms of $C_{ij}^{HS}(r)$ as follows:

$$-C_{ij}^{HS}(r) = \begin{cases} a_i & r < \lambda_{ij} \\ a_{ij} + b_{ij}r + dr^3 + \dfrac{f_{ij}}{r} & \lambda_{ij} < r < \sigma_{ij} \\ 0 & r > \sigma_{ij} \end{cases} \tag{5}$$

where:

$$\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2}, \quad \lambda_{ij} = \frac{(\sigma_j - \sigma_i)}{2}, \quad a_{ij} = \frac{(a_i + a_j)}{2} \quad \text{and} \quad b_{ij} = \frac{(b_i + b_j)}{2}$$

σ_i is the hard sphere diameter used for the ith species. The other coefficients are given by Hiroike and Hoshino[14,15].

2.3 Direct correlation functions in the case of square-well (or shouldered) potential

In this work, the calculation is done with a square-well (or a shouldered) potential as a perturbation over a hard sphere mixture:

$$V_{ij}(r) = \begin{cases} \infty & r < \sigma_{ij} \\ \varepsilon_{ij} & \sigma_{ij} < r < A_{ij}\sigma_{ij} \\ 0 & r > A_{ij}\sigma_{ij} \end{cases} \tag{6}$$

σ_{ii}, ε_{ii} and $\sigma_{ii}(A_{ii} - 1)$ stand for the hard sphere diameter, height (or depth if ε is negative) and width of the model potential used for the ith species, respectively. The mixed parameters $(i \neq j)$ are determined by assuming the Lorentz-Berthelot rules. Thus we obtain:

$$\sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2} \quad \text{(additivity assumed)}$$

$$\varepsilon_{\text{Ni}-\text{Si}} = -(|\varepsilon_{\text{Ni}-\text{Ni}}\varepsilon_{\text{Si}-\text{Si}}|)^{1/2}, \quad \varepsilon_{\text{Al}-\text{Ni}} = -(|\varepsilon_{\text{Ni}-\text{Ni}}\varepsilon_{\text{Al}-\text{Al}}|)^{1/2}$$

$$\varepsilon_{\text{Al}-\text{Si}} = 0 \tag{7}$$

$$A_{ij} = \frac{(A_{ii}\sigma_i + A_{jj}\sigma_j)}{(\sigma_i + \sigma_j)}$$

The choice of the sign of ε_{ij} is discussed in Section III. We consider the usual approximation[9,10,11] for $C_{ij}(r)$ and write:

$$C_{ij}(r) = \begin{cases} C_{ij}^{HS}(r) & 0 \leqslant r < \sigma_{ij} \\ -\beta V_{ij}(r) = -\beta\varepsilon_{ij} & \sigma_{ij} \leqslant r \leqslant A_{ij}\sigma_{ij} \\ 0 & r > A_{ij}\sigma_{ij} \end{cases} \tag{8}$$

where $\beta = 1/k_B T$ and $C_{ij}^{HS}(r)$ stands for the hard sphere PY solution[14]. We obtained straightforwardly the Fourier transforms $C_{ij}(q)$ from equations (5) and (8):

$$\sqrt{\rho_i\rho_j}\, C_{ij}(q) = \frac{4\pi\sqrt{\rho_i\rho_j}}{q^2} \left\{ a_i \left[\lambda_{ij} \cos q\,\lambda_{ij} - \frac{1}{q} \sin q\,\lambda_{ij} \right] + f_{ij}\left[\cos q\,\sigma_{ij} - \cos q\,\lambda_{ij}\right] \right.$$

$$+ a_{ij} \left[\sigma_{ij} \cos q\, \sigma_{ij} - \lambda_{ij} \cos q\, \lambda_{ij} - \frac{1}{q}(\sin q\, \sigma_{ij} - \sin q\, \lambda_{ij}) \right]$$

$$+ b_{ij} \left[\sigma_{ij}^2 \cos q\, \sigma_{ij} - \lambda_{ij}^2 \cos q\, \lambda_{ij} - \frac{2}{q}(\sigma_{ij} \sin q\, \sigma_{ij} - \lambda_{ij} \sin q\, \lambda_{ij}) \right.$$

$$\left. - \frac{2}{q^2}(\cos q\, \sigma_{ij} - \cos q\, \lambda_{ij}) \right]$$

$$+ d \left[\sigma_{ij}^4 \cos q\, \sigma_{ij} - \lambda^4{}_{ij} \cos q\, \lambda_{ij} - \frac{4}{q}(\sigma_{ij}^3 \sin q\, \sigma_{ij} - \lambda_{ij}^3 \sin q\, \lambda_{ij}) \right. \tag{9}$$

$$- \frac{12}{q^2}(\sigma_{ij}^2 \cos q\, \sigma_{ij} - \lambda_{ij}^2 \cos q\, \lambda_{ij}) + \frac{24}{q^3}(\sigma_{ij} \sin q\, \sigma_{ij} - \lambda_{ij} \sin q\, \lambda_{ij})$$

$$\left. \left. + \frac{24}{q^4}(\cos q\, \sigma_{ij} - \cos q\, \lambda_{ij}) \right] \right\}$$

$$+ \frac{4\pi \sqrt{\rho_i \rho_j}\, \varepsilon_{ij}}{q^3} \frac{1}{k_B T}(A_{ij}\, q\sigma_{ij} \cos(A_{ij} q \sigma_{ij}) - \sin(A_{ij} q \sigma_{ij})$$

$$- q\sigma_{ij} \cos(q\sigma_{ij}) + \sin(q\sigma_{ij}))$$

2.4 Determination of the parameters of the potential

The parameters σ_i, ε_{ii} and A_{ii} of the effective potential model have been fitted on the experimental structure factors of the pure liquid metals near the melting point[17] using the simplex method. We obtain:

$$\varepsilon_{Al-Al}/k_B = -94.02\,K \quad \varepsilon_{Ni-Ni}/k_B = -66.49\,K \quad \varepsilon_{Si-Si}/k_B = 182.46\,K$$

$$A_{Al-Al} = 1.89 \qquad A_{Ni-Ni} = 3.03 \qquad A_{Si-Si} = 3.29$$

$$\sigma_{Al} = 2.55\,\text{Å} \qquad \sigma_{Ni} = 2.20\,\text{Å} \qquad \sigma_{Si} = 2.14\,\text{Å}$$

We can observe that the parameter ε for silicon corresponds to a repulsive potential while it is attractive for aluminum and nickel. None of these adjusted parameters looks unphysical, therefore they have been used and kept constant for the binary and ternary alloys.

2.5 Theoretical total structure factor

The total structure factor of the ternary alloy from the neutron diffraction experiment is given by a combination of (A-L) partial structure factors:

$$S(q) = \sum_{i=1}^{3} \sum_{j=1}^{3} \sqrt{x_i x_j}\, \frac{(b_n)_i (b_n)_j}{\langle (b_n)^2 \rangle} S_{ij}(q) \tag{10}$$

where x_i is the concentration of the ith species and $(b_n)_i$ is the neutron scattering amplitude. $\langle b_n \rangle$ is a concentration weighted amplitude.

$$\langle (b_n)^2 \rangle = \sum_{i=1}^{3} x_i (b_n)_i^2$$

The values of b are taken from [18]:

$$(b_n)_{Si} = 0.4149.10^{-8}\,\text{cm} \quad (b_n)_{Ni} = 1.03.10^{-8}\,\text{cm} \quad (b_n)_{Al} = 0.3449.10^{-8}\,\text{cm}$$

3   RESULTS AND DISCUSSION

Recently, Maret *et al.*[1] measured, with the isotopic substitution method, the partial structure factors of $Al_{80}Ni_{20}$ and showed that the chemical short-range order exists

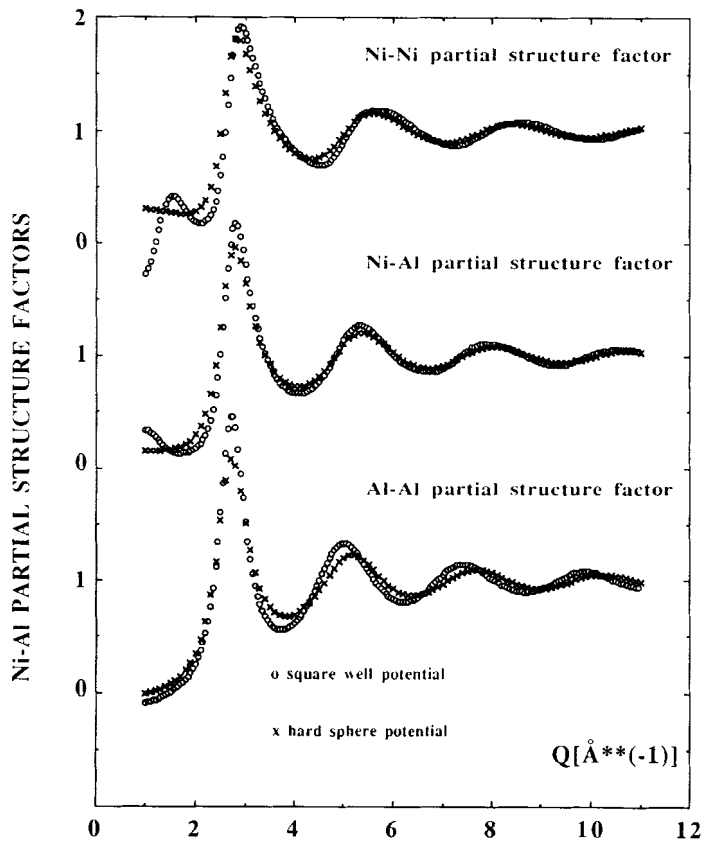**Figure 1**   Calculated partial structure factor of liquid $Al_{80}Ni_{20}$ at 1250 K with hard sphere and square well hard sphere ones.

and is more pronounced than in $Al_{80}[Mn_x(FeCr)_{1-x}]_{20}$. This was confirmed by the fact that the heat of formation is more negative for Al_xNi_{1-x} alloys, and indicates also the existence of a higher degree of chemical short range order. The existence of a prepeak in a_{Ni-Ni} and a preminimum in a_{Ni-Al} is the sign of superstructure effects due to predominance of heteroatomic interaction. Such an argument is in favour of the introduction of attraction between dissimiliar species which are, in the present work,modelized by a simple square well. Our calculated partial structure factors are represented on Figure 1 and can be compared with Figure 6 of Maret et al.[1] The same general features as those of the experimental partial structure factors are obtained.

In particular, Maret et al.[1] found a prepeak in a_{Ni-Ni} at $1.86 Å^{-1}$. From our calculations and our parameters, such a prepeak is found at $1.55 Å^{-1}$. In a_{Ni-Ni}, the experimental curve shows a preminimum at $2.3 Å^{-1}$. This value is higher than the calculated one which is at $1.8 Å^{-1}$. This difference can be due to the fact that the parameters of the model have been kept constant from the pure metals determination, and that the Lorentz-Berthelot rule has been assumed. Nevertheless, it is worth noting that in spite of such shortcoming, the model predicts both a prepeak for a_{Ni-Ni} and a
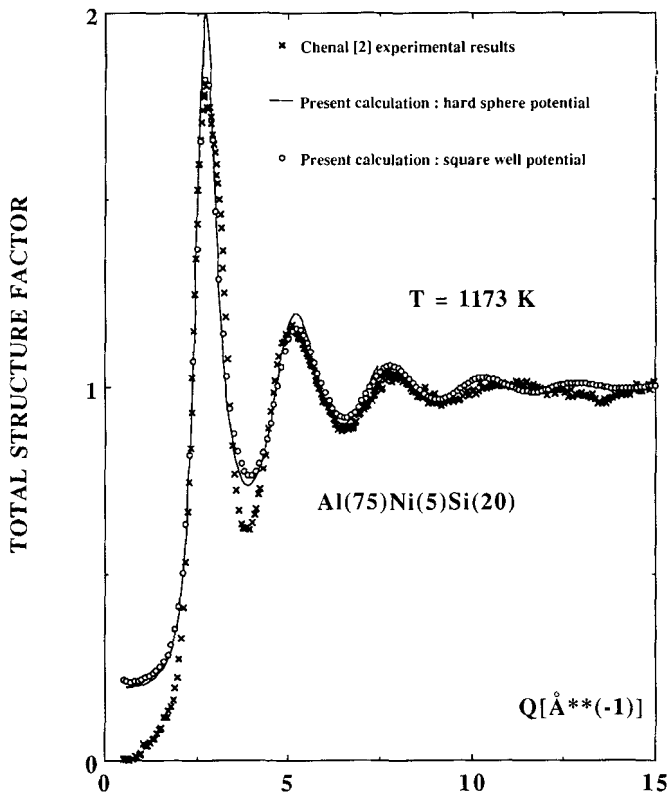

Figure 2 Chenal[2] total experimental structure factor of liquid $Al_{75}Ni_5Si_{20}$ at 1173 K compared to our calculated hard sphere and square well hard sphere ones.

preminimum for a_{Ni-Al}. Moreover it is worth noting that the parameters of the pure metals are able to predict qualitatively well the structure factor of the alloy. Chenal[2] measured the structure factor of five Al—Ni—Si ternary alloys at 100 K above the melting point including binary $Al_{80}Ni_{20}$. We selected two ternary alloys $Al_{65}Ni_{15}Si_{20}$ and $Al_{75}Ni_5Si_{20}$ respectively inside and outside the amorphisation domain. On Chenal experiments[2], it is observed the presence of a prepeak when the nickel concentration reaches 15 to 20 at.% of Ni. Such a prepeak (at constant nickel concentration) is less important than in the binary $Al_{80}Ni_{20}$ liquid alloy. We calculated the total structure factor of $Al_{75}Ni_5Si_{20}$ and of $Al_{65}Ni_{15}Si_{20}$. The Lorentz-Berthelot rule is ambiguous for ε_{ij} if one potential is attractive and the other repulsive. We examined the enthalpy of formation (ΔH_{for}^{max}) of binary Ni—Si, Al—Ni and Al—Si alloys. They are respectively of -66.88 kJ/mole, $-58,8$ kJ/mole and $-2,197$ kJ/mole[19,20,21]. We therefore neglect the interaction between aluminum and silicon (i.e. we take $\varepsilon_{Al-Si} = 0$). We assumed that the interactions Ni/Al and Ni/Si are described by the Lorentz-Berthelot rules and choose the negative value for Ni/Si. The calculated structure factors are plotted on Figure 2 and Figure 3 respectively, and are compared to Chenal's[2] experimental values. In the 5 at.% Ni alloy (Fig. 2), no prepeak is observed in the total structure
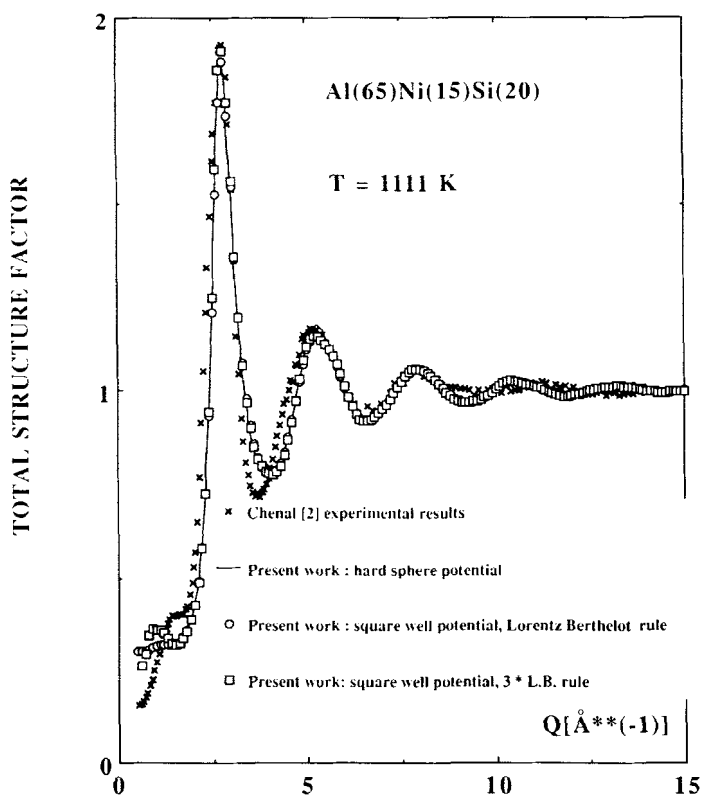

Figure 3 Chenal[2] total experimental structure factor of liquid $Al_{65}Ni_{15}Si_{20}$ at 1111 K compared to our calculated hard sphere and square well hard sphere ones.

values. In the 5 at.% Ni alloy (Fig. 2), no prepeak is observed in the total structure factor. The ternary hard sphere total structure factor reproduces well the position of the first, second and third peak but not the amplitude. When the square well potential model is considered, the same agreement for the positions of the peaks is obtained and the agreement with the amplitude is improved (except the first minimum). In the case of 15 at.% Ni alloy (Fig. 3), both hard sphere and square well potential models describe reasonably the experimental structure factor. In the low q region, a prepeak is obtained with square well potential but never with hard spheres (Fig. 4). However, Lorentz-Berthelot rule gives only a small prepic, it can be enhanced if the ε_{Al-Ni} term is more attractive. For example we plot on Figures 3 and 4 the curve obtained if ε_{Al-Ni} is taken to be three times that given by the Lorentz-Berthelot rule. The prepic is more marked. To understand which term is the preeminent one in the total structure factor, we increased arbitrarily the neutron scattering amplitude $(b_n)_i$. Doing so, we see better the effect of the corresponding atom and the binary interactions (with this atom) which have an effect on the total structure factor. We observed that increasing $(b_n)_{Al}$ has no effect on the prepeak. We believe that the size of the hard sphere is also important since Ni and
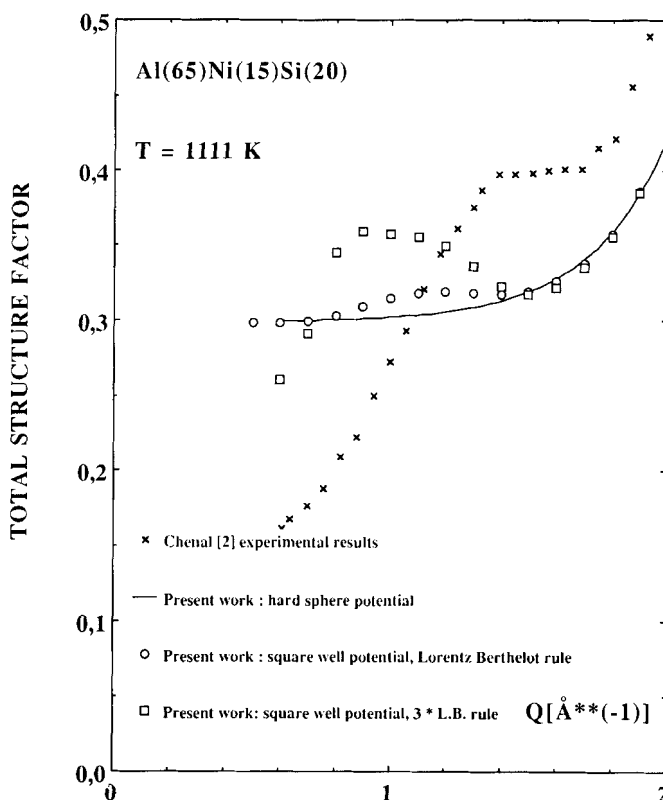

Figure 4   Hard sphere structure factor of liquid $Al_{75}Ni_5Si_{20}$ at 1111 K in the low q region compared to the square well one.

$(b_n)_{Ni}$ and $(b_n)_{Si}$ increases the prepeak of the total structure factor. This is surprising since ε is positive for silicon and negative for nickel. The sign of ε_{ii} is not necessarily in contradiction with the observed effect since the important term is the depth of the heteroatom parameter ε_{ij} ($i \neq j$). The hard sphere model with additive hard spheres has been always found unable to predict any prepeak in the small q range. On the other hand, introducing the square well interactions gives qualitatively such a feature.

CONCLUSION

Calculations using square well potential have, to our knowledge, been used for the first time for ternary alloys. The structure factor of binary and ternary liquid alloys with strong chemical short range order at amorphous compositions can be qualitatively explained on the basis of multicomponent hard sphere model and square well interatomic potentials. The attraction between heteroatoms has been modelized assuming several crude approximation such as square well potentials, and Lorentz-Berthelot rules. Therefore one could expect further improvement of the model since attraction has not been discussed here independently of the Lorentz-Berthelot rules.

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