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The Influence of Medium- and Long-range Forces on the Structure of Liquid Binary Alloys

II Concentration-dependent Changes in the Topological-short-range Order of Al-Ge Alloys

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The generalized optimized random-phase approximation (ORPA) for binary mixtures is applied to an investigation of the structure of liquid Al-Ge alloys. We show that the liquid structure and its variation with composition is strongly influenced by medium- and long-range interatomic forces. The short-range structure is characterized by almost concentration independent coordination numbers for alloys containing up to 40 atomic percent Ge. At about 50 atomic percent Ge the coordination changes to smaller coordination numbers characteristic for liquid Ge. The long-range structure is rather complex and is determined by the interplay of three different length scales: the effective hard-core diameters of the two atomic species and the Friedel wavelength of the oscillations in the interatomic potentials.

PACS classifications: 61.25.Mv, 61.20.Gy, 61.45. + s

Key Words: Liquid Al-Ge alloys, optimized random-phase approximation (ORPA), medium- and long-range forces.

1 INTRODUCTION

Liquid binary alloys are usually classified according to their chemical short-range order (CSRO): we distinguish between nearly ideal mixtures (with a random distribution of the atomic constituents), alloys with a tendency to compound formation (they show a preference for the

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formation of unlike-atom pairs), and alloys with a tendency to clustering and phase separation (where like atoms tend to cluster together).¹ This classification fails if at least one of the components is an element from groups IV or V with a non-metallic behaviour in the crystalline state. Examples studied by diffraction techniques are Bi-Sb alloys² and Al-Si melts.³ Here large concentration-dependent changes in the topological short-range order (TSRO) are observed. In pure Al the coordination number (obtained by integrating the radial distribution function up to the first minimum) is $N_c \sim 10.2$, in pure Si one finds $N_c \sim 6.4$. These values are rather close to those in fcc Al ($N_c = 12$), and in the metallic high-pressure polymorph of Si with the β -tin structure ($N_c = 6$). This suggests that the topological short-range order is rather different in the two liquid elements

For the pure liquid metals we have been able to show^{4,5} that the characteristic changes in the liquid structure along the series Na-Mg-Al-Si arise from the systematic variation of the interatomic interactions with electron density and pseudopotential.^{6,7} For Na, Mg and Al the form of the interatomic potential is found to be compatible with a hard-sphere like arrangement of the atoms. The more complex structures of the light polyvalent metals (Si, Ge, Ga) have been shown to arise from the interplay of two characteristic distances: the effective diameter of the hard repulsive core expressing the geometrical requirements of sphere packing and the Friedel wavelength of the oscillatory part of the potentials characterizing the electronic effects in the metallic bonding.

In the present paper we extend these investigations to liquid Al-Ge alloys. Our aim is to study the concentration-dependent changes in the topological short-range order. As for the pure metals, the investigations are based on pseudo-potential derived interatomic forces and on the optimized random-phase approximation for the calculation of the structure functions of the liquid alloy. We decided to investigate the Al-Ge system rather than the Al-Si system for which diffraction data are available,³ because we expect the "visibility" of the structural changes to be better in this alloy. For Al and Si, the static structure factors have their peak at nearly the same wavenumber ($Q_p = 1.43$ a.u. for Al and Si^{3,8}). Therefore, the main peaks of the partial structure factors exactly superpose in the alloy. For Ge, we have $Q_p = 1.37$ a.u. and we expect to see a more distinct manifestation of the change in TSRO in the composite structure factors.

We find that the alloy has a rather complicated structure. It is determined by three different length scales: the hard-core diameters σ_{Al} and σ_{Ge} , and the Friedel wavelength λ_F of the valence-electron gas. All three length scales manifest themselves in all three partial structure factors.

2 THEORY

2.1 Interatomic forces

The effective interatomic potentials have been calculated in second order perturbation theory, using the Ashcroft empty core potential⁹ (the core radius R_c is determined from the zero-pressure condition at $T = 0$ K, $R_c = 1.12$ a.u. for Al and $R_c = 1.03$ a.u. for Ge) and the Ichimaru-Utsumi¹⁰ screening function. For the pure metals an ORPA-calculation of the liquid structure based on these interatomic potentials yields perfect agreement with the experimental diffraction data.^{4,5,11} Figure 1 shows the interatomic potentials in Al-Ge alloys of different compositions. We find that there are only rather small changes with composition and that the differences between the Al-Al and Ge-Ge interactions are rather small. The important thing is to remember that the system is not in equilibrium under the action of the pair forces alone. The equilibrium density is the result of the interplay between volume and pair forces.¹ For pure Al, this places the average nearest-neighbour distance in a close-packed (crystalline or liquid) structure close to the minimum in the pair interaction—in that case a close-packed arrangement will be stable. For pure Ge, the nearest neighbour distance for close-packing would fall on the maximum of the pair-potential—clearly in that case a more open structure would be energetically more favourable.^{4,6} Here we want to study the variation of these structural effects with composition.

2.2 From the interatomic potential to the structure of the alloy

The optimized random phase approximation (ORPA) for the calculation of the partial pair correlation functions of a binary alloy has been described in the first paper of this series (Ref. 12—hereafter this paper will be referred to as I). The interatomic potentials are split into a short-range repulsive part and a long-range oscillatory part. The Weeks-Chandler-Anderson (WCA) expansion is used to account for the deviations of the soft repulsive forces from a hard sphere form. The effect of the long-range forces is treated in the ORPA.

The crucial point is to find a way to split the potential such that we can use a binary mixture of additive (i.e. $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$) hard spheres of different diameters σ_{AA} and σ_{BB} as a reference system. The procedure proposed in I is the following: the potentials $\Phi_{ii}(R)$ for like-atom interactions are separated at the position of the first minimum R_{ii} (if—as is the case for Ge—the first minimum degenerates into an inflection point, we take the inflection point instead of the minimum). We determine the effective hard-sphere diameters σ_{AA} , σ_{BB} such that the blip-function conditions (Eq. (9) of I) are satisfied for like-atom

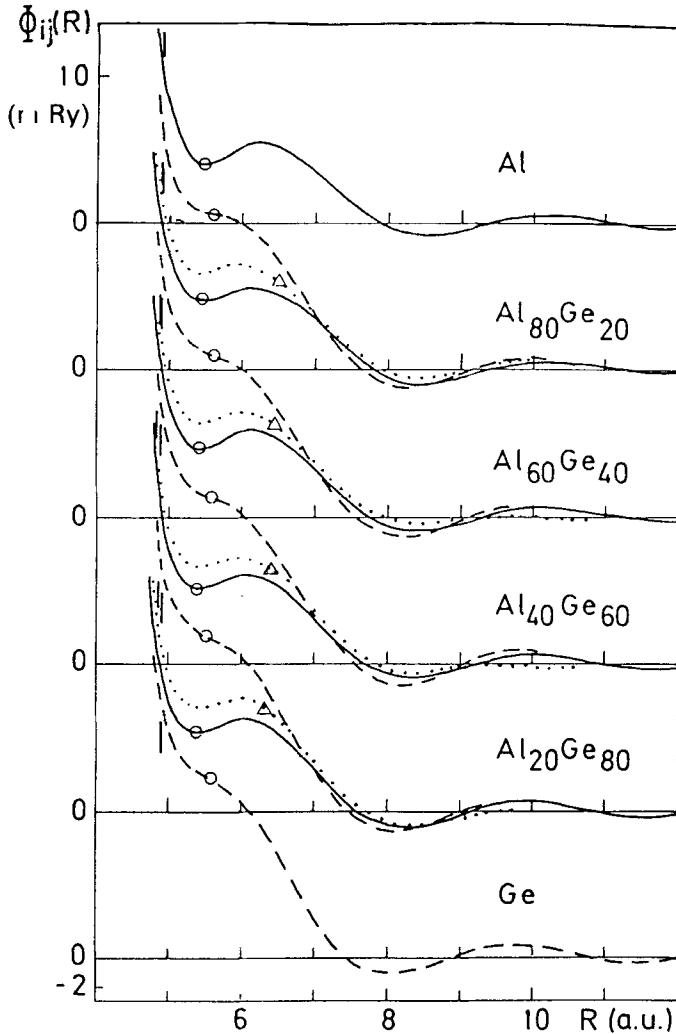


Figure 1 The effective interatomic interactions $\Phi_{ij}(R)$ in Al-Ge alloys and in pure Al and Ge. The open circles mark the minimum, resp. the inflection point at which the like-atom interactions are separated, the triangle marks the separation distance R_{12} for the unlike-atom interactions. The vertical bars indicate the effective hard-sphere diameters σ_{ij} .

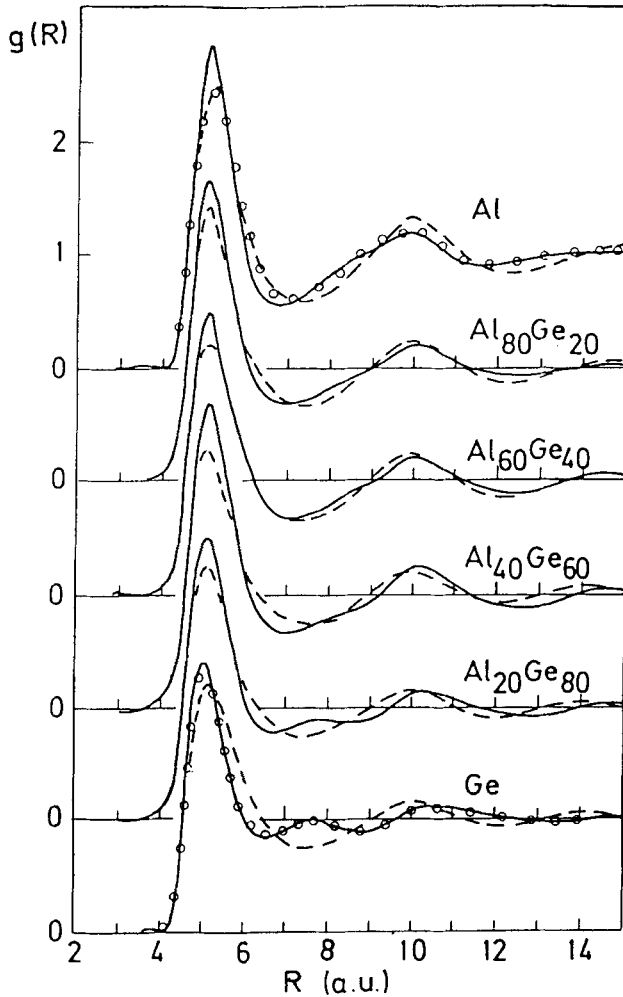


Figure 2 Composite (neutron-weighted) pair correlation functions of Al, Ge and Al-Ge alloys, calculated with the WCA (soft repulsive forces only, dashed lines) and the ORPA methods (full potential, full lines). For the pure elements the experimental data of Waseda⁸ are shown for comparison. Note that the neutron-scattering lengths are $b_{\text{Al}} = 0.35$, $b_{\text{Ge}} = 0.82$.

interactions. Then we set $\sigma_{AB} = (\sigma_{AA} + \sigma_{BB})/2$ and vary the distance R_{AB} at which we separate $\Phi_{AB}(R)$ such that the blip function condition is also satisfied for unlike-atom interactions. The points at which the potentials are separated and the effective hard-core diameters resulting from the WCA procedure are indicated in Figure 1. The effective hard-core size ratio is very close to unity.

For the solution of the coupled ORPA equations we follow again the variational procedure described in I.

3 RESULTS

We have solved the ORPA-equations for pure Al and Ge, and for $\text{Al}_c\text{Ge}_{1-c}$ alloys with $c = 0.8, 0.6, 0.4,$ and 0.2 at $T = 1250$ K. As the density is known only for the pure metals,⁸ the density of the alloy was obtained by interpolation of the atomic volume. We expect the error caused by the interpolation to be very small, the theoretically predicted deviation from Zen's law being of the order of 0.1 percent.¹³

The composite (neutron-weighted) pair correlation functions are shown in Figure 2. We observe a smooth variation with composition: the ratio of the positions of the two main peaks R_{II}/R_I shifts from a hard-sphere like value in Al ($R_{II}/R_I = 1.91$) to a definitely larger value ($R_{II}/R_I = 2.04$) in Ge, an intermediate maximum begins to appear at ~ 50 percent Ge. The height of the main peak is reduced, and the amplitudes of the higher order peaks are strongly reduced by the addition of Ge. By comparing the WCA results (soft repulsive interactions only) with the ORPA results (full potential), we find that the characteristic changes in the liquid structure are triggered by the medium and long-range oscillations in the pair interactions. The intermediate maximum appears precisely at the position of the minimum in the pair potential, and the shift of the second maximum also goes into the direction of the next minimum of the pair potential. Note that even pure Al is not as hard-sphere like as it is often considered to be. The predicted deviations from a soft-sphere picture agree with experiment, although they appear to be slightly exaggerated by the calculation.

The characteristic features in the structure of the alloy appear perhaps even more distinctly in the static structure factor (Figure 3). Already in pure Al we observe a broadening and a slight shift of the main peak of $S(k)$, in the experiment as well as in the ORPA calculation. On adding Ge to Al, distinct shoulders appear on both sides of the main peak, that on the left side develops into the main Ge-peak, that on the

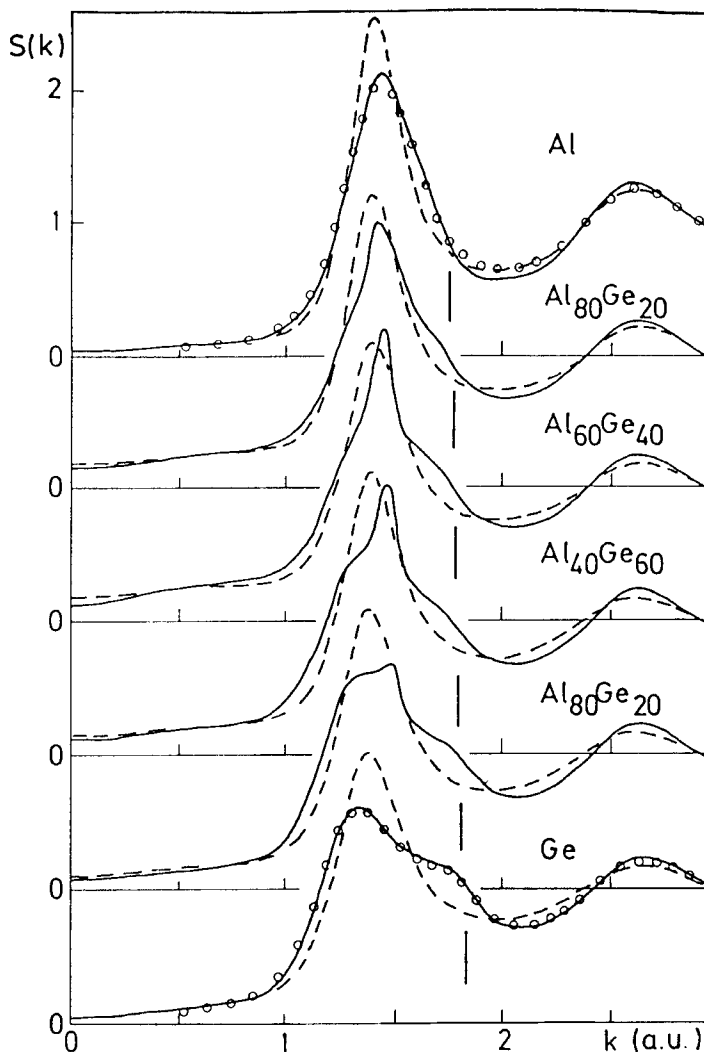


Figure 3 Composite (neutron weighted) static structure factors of Al, Ge and Al-Ge alloys. Cf. Figure 2. The vertical bars indicate the value of $k = 2k_F$.

right side correlates with $2k_F$. Even at a composition of 80 percent Ge, we still predict a distinct signature of the Al peak.

Figures 4 and 5 demonstrate that the partial correlation functions and structure factors display the same details. A peak near $k \sim 1.45$ a.u. exists even in the Ge-Ge structure factors, the Al structure factors have shoulders on both sides if the Ge concentration is sufficiently high. In

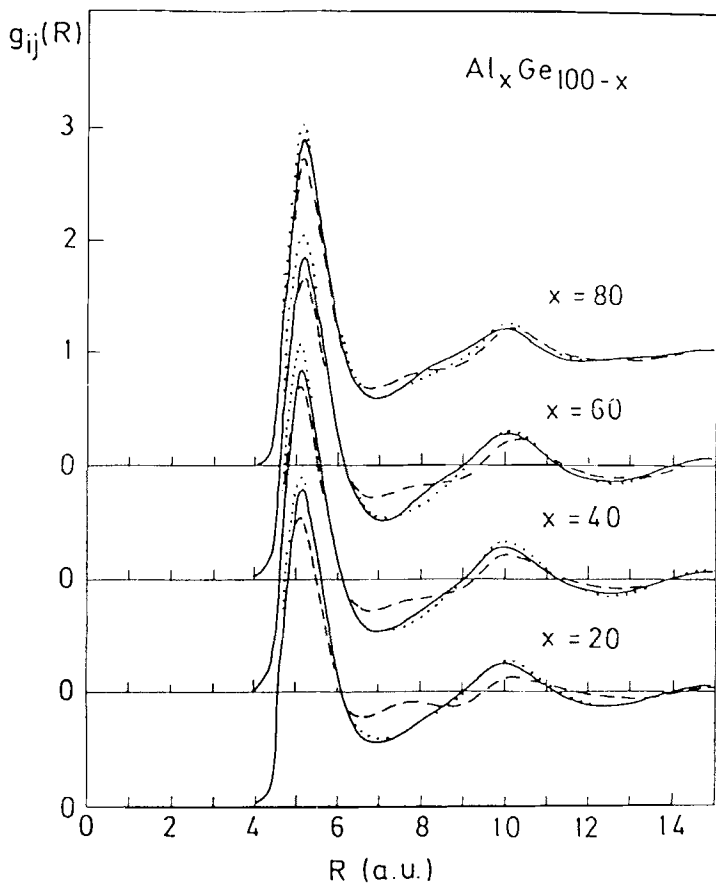


Figure 4 Partial pair correlation functions of Al-Ge alloys, calculated in the ORPA; full line—Al-Al, dotted line—Al-Ge, dashed line—Ge-Ge.

the partial pair correlation functions, the intermediate maximum near $R \sim 8.0$ a.u. appears only in the Ge-Ge correlation function.

As a more technical point we note that the partial static structure factors do not display the small anomalies near $k \sim 0.6 \times Q_p$ (Q_p being the position of the main peak) we had found in the K-Cs alloys (see the discussion in I). This is certainly related to the fact that the effective size-ratio is very close to unity and that $\Phi_{12}(R)$ is very small in the region $\sigma_{12} \leq R \leq R_{12}$ (see Figure 1).

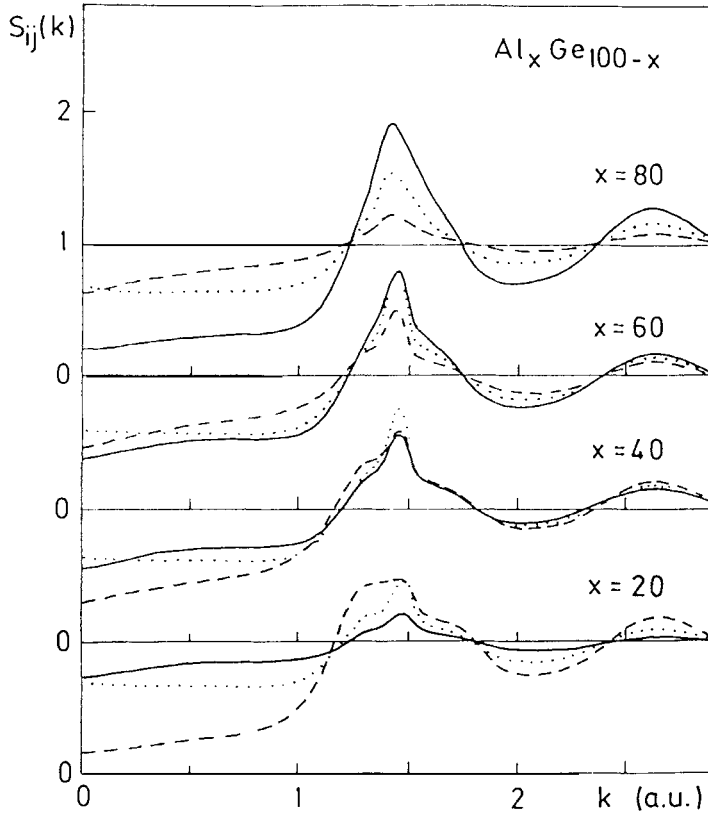


Figure 5 Partial static structure factors of Al-Ge alloys; same symbols as Figure 4.

CONCLUSIONS

From the calculated pair correlation functions, the coordination number can be derived by integrating the pair distribution function $4\pi R^2 g(R) \cdot n$ up to the minimum between the first and the second maximum. The total coordination numbers calculated by integrating over the composite pair distribution function are shown in Figure 6. In accordance with the work of Gabathuler *et al.* on Al-Si alloys³ we find that the total coordination number N_c is nearly unchanged for alloys with up to ~ 40 atomic percent Ge, and changes to lower coordination numbers typical for the Ge-rich alloys at about the equiatomic composition. The transition is not as sharp as suggested by the data of

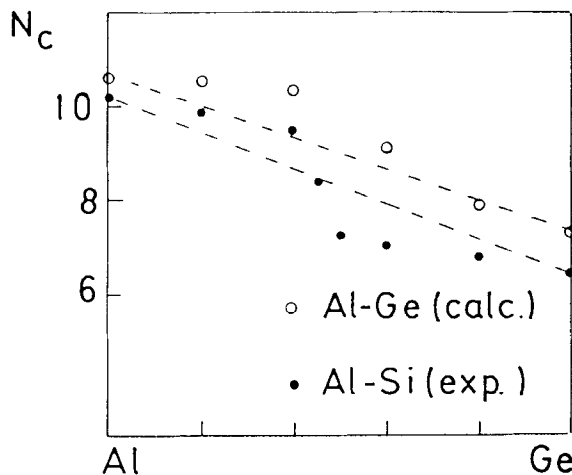


Figure 6 Total coordination numbers derived from the composite pair correlation functions: Al-Ge (calculated), circles—Al-Si (exp., Ref. 3).

Gabathuler *et al.*³ However, we should not forget that the definition of the coordination number is not a very precise one. Most of the changes in N_c arise from the shift of the minimum to smaller distances (which is in turn a consequence of the appearance of the intermediate maximum)—so a small variation in the correlation function might entail a rather large one in the coordination number.

The characteristic form of the partial static structure factors demonstrates that the long-range-structure of the Al-Ge alloys is determined by the interplay of *three* different length scales: the effective atomic diameters of Al and Ge, and the Friedel wavelength $\lambda_F = 2\pi/2k_F$ of the long-range oscillations in the interatomic potentials. This would seem to be surprising at first sight, but of course the distance between two Al atoms depends on the size of the Ge atoms which could lie between the Al atoms as well as on the size of the Al-atoms themselves. However, it requires rather harshly repulsive short range forces for these correlations to show up so clearly as they do in Al-Ge alloys. In the alkali-alloys for example, these correlations are smeared out because of the softness of the interatomic interactions (in that connection it is worthwhile to point out that the full width at half maximum of $g(R)$ is about 20 percent in the Al-Ge alloys, and about 30 percent in a typical alkali alloy, in units of the nearest-neighbour distance).

To summarize, we have shown that a simple picture based on volume and pair forces yields a reasonable description of the composition-dependent variation of the structure of liquid Al-Ge alloys. Our

approach should supersede earlier interpretations of the experimental data based on micro- or quasicrystalline models. Preliminary results suggest that the improved description of the liquid structure also yields improved results for the composition variation of other properties, e.g. for electrical transport. We hope that our work will stimulate an experimental investigation of liquid Al-Ge alloys.

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