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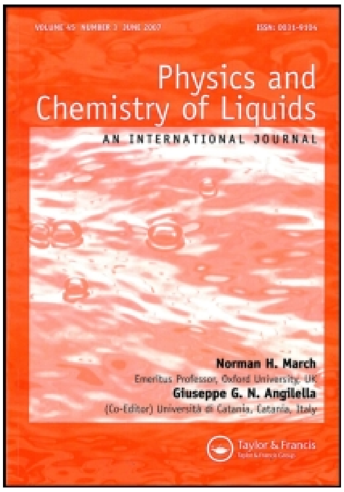

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Structure Factors of Liquids Containing Chemical Complexes[†]

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A theory of the three partial structure factors of an A–B alloy containing $A_\mu B_\nu$ complexes is set up as composites of the structure factors for the three component system. Applying the theory to liquid Ga with Ga_2 complexes, the shoulder observed on the liquid structure factor at 50° C is interpreted as arising from bond-centre (Ga_2)–Ga correlations.

1 INTRODUCTION

Most theoretical treatments of the structure factors of liquid metals and their alloys start out from the assumption of central pair potentials. However, there is compelling evidence from the phase diagrams and other properties of certain binary alloys that chemical complexes can form, even when bonding forces are greatly weakened by metallic screening.

Therefore, in this paper, we present the theory of partial structure factors in A–B alloys in which chemical complexes $A_\mu B_\nu$ occur with a concentration to be determined from the law of mass action, as discussed by Bhatia and Hargrove.[3] We shall do this by calculating the X-ray scattered intensity I(K) from the alloy: the modifications required to pass to neutron scattering are obvious.

2 MODEL OF CHARGE DENSITY AND X-RAY SCATTERING

Following standard practice in the case of crystalline materials, we shall assume that we can associate with A and B nuclei, whether free, or bound

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in complexes $A_\mu B_\nu$, localized spherical densities $\rho_A(r)$ and $\rho_B(r)$. Let the free A atoms be at positions $\mathbf{l}_1$, B at $\mathbf{l}_2$ while the "centres" of $A_\mu B_\nu$ are at **L**. Then, measured from **L**, the μ A's in the complex are at positions $\mathbf{R}^L_{1i}$, $i = 1$ to μ, the ν B's being at $\mathbf{R}^L_{2j}$, $j = 1$ to ν. For such a fixed configuration of nuclei, the total electron density is represented by

$$\rho(\mathbf{r}) = \sum_{\mathbf{l}_1} \rho_A(\mathbf{r} - \mathbf{l}_1) + \sum_{\mathbf{l}_2} \rho_B(\mathbf{r} - \mathbf{l}_2) + \sum_{\mathbf{L}} \left[\sum_{i=1}^{\mu} \rho_A(\mathbf{r} - \mathbf{L} - \mathbf{R}^L_{1i}) + \sum_{j=1}^{\nu} \rho_B(\mathbf{r} - \mathbf{L} - \mathbf{R}^L_{2j}) \right]. \tag{1}$$

The X-ray scattering factor $f(K)$, given by $\int \rho(\mathbf{r}) \exp(i\mathbf{K}\cdot\mathbf{r})\, d\mathbf{r}$ is then obtained in terms of the atomic scattering factors $f_A(K)$ and $f_B(K)$ as

$$f(K) = f_A(K) F_A + f_B(K) F_B \tag{2}$$

where

$$F_A(K) = \sum_{\mathbf{l}_1} \exp(i\mathbf{K}\cdot\mathbf{l}_1) + \sum_{\mathbf{L}} \sum_{i=1}^{\mu} \exp(i\mathbf{K}\cdot\{\mathbf{L} + \mathbf{R}^L_{1i}\}) \tag{3}$$

and

$$F_B(K) = \sum_{\mathbf{l}_2} \exp(i\mathbf{K}\cdot\mathbf{l}_2) + \sum_{\mathbf{L}} \sum_{j=1}^{\nu} \exp(i\mathbf{K}\cdot\{\mathbf{L} + \mathbf{R}^L_{2j}\}). \tag{4}$$

Forming the X-ray intensity $I(K)$ as $|f(K)|^2$ and taking the liquid average, the usual partial structure factors of a two-component system are readily identified as

$$\left.\begin{aligned} N_A S_{AA} &= \langle F_A F_A^* \rangle \\ 2(N_A N_B)^{\frac{1}{2}} S_{AB} &= \langle F_A F_B^* + \text{complex conjugate} \rangle \\ N_B S_{BB} &= \langle F_B F_B^* \rangle \end{aligned}\right\}, \tag{5}$$

where N_A and N_B are the total numbers of A and B atoms in the alloy.

It is evident from Eqs. (3–5) that if we wish to compute these partial structure factors, say in Mg–Bi, near the concentration of the intermetallic compound, then we must have correlations between the $\mathbf{l}_1$'s, $\mathbf{l}_2$'s, the complex centres **L** and the cross-correlations, as zeroth order input information. At the next stage, angular correlations would need to be considered. However, even "excluded volume" effects have not yet been calculated for a 3-component hard sphere mixture, though we are currently attempting this by the method based on the singularities in the structure factors, which has been developed in another place.[5] When such information becomes available, the above equations afford a route for estimating the composite structure factors S_{AA}, S_{BB} and S_{AB}, which obviously contain through their dependence on the concentration of complexes (i.e. on temperature) the binding energy of the complex $A_\mu B_\nu$. Because this lack of information precludes a calculation on Mg–Bi say, which we regard as the major objective of the present theory, we shall illustrate the method below by discussing pure liquid Ga.

3 ILLUSTRATIVE EXAMPLE: LIQUID GA

While complexes are widely accepted as existing in a material like Mg–Bi, the case of Ga is more open to discussion, but there have been numerous suggestions earlier that Ga_2 complexes can exist in the pure liquid. In this case, with the notation Ga $\equiv$ 1, $Ga_2 \equiv 2$, the above equations immediately lead to the X-ray scattered intensity as

$$\begin{aligned} I(K) &= f^2(K)\left[N_1 S_{11}(K) + 2(N_1 N_2)^{\frac{1}{2}}\overline{S_{12}(K)} + N_2\overline{S_{22}(K)}\right] \\ &\equiv N f^2(K)\, S(K) \end{aligned} \tag{6}$$

where f(K) is the atomic scattering factor of Ga and, explicitly, in an obvious notation

$$2(N_1 N_2)^{\frac{1}{2}}\overline{S_{12}(K)} = \langle \sum_{l,L} \exp\,(i\mathbf{K}\cdot \mathbf{l} - \mathbf{L})\, 2\cos \mathbf{K}\cdot\mathbf{R}_L + \text{c.c.}\rangle \tag{7}$$

and

$$N_2\overline{S_{22}(K)} = \langle |\sum_{L} \exp\,(i\mathbf{K}\cdot\mathbf{L})\, 2\cos \mathbf{K}\cdot\mathbf{R}_L|^2\rangle \tag{8}$$

where the separation in Ga_2 has been taken to be 2**R** for convenience.

We can safely assume small concentrations of Ga_2 complexes in interpreting the structure data of Ascarelli[1] and then, at least in the interesting region around the first peak of S(K) in Ga the new structural element beyond S_{11} is $\overline{S_{12}(K)}$. Assuming for a moment a fixed Ga_2 bond length 2R, $\overline{S_{12}(K)}$ can be written more explicitly as

$$\overline{S_{12}(K)} = 2(\rho_1\rho_2)^{\frac{1}{2}}\int dr\, d\Omega\,[g_{12}(r) - 1]\, P(\Omega, \mathbf{r}) \cos \mathbf{K}\cdot\mathbf{r} \cos \mathbf{K}\cdot\mathbf{R}, \tag{9}$$

ρ_1 and ρ_2 now being number densities while $g_{12}(r)$ is the bond-centre (Ga_2)–Ga correlation function. Finally, in (9), $P(\Omega, \mathbf{r})$ is the probability of a solid angle Ω between the axis of a Ga_2 complex and the vector **r** joining its centre to a free Ga atom. Of course, with relatively weak bonding, we must eventually average over a distribution of R, to account for vibrational fluctuations. If we now define a function

$$F(KR, \mathbf{r}) = \int d\Omega\, P(\Omega, \mathbf{r}) \cos \mathbf{K}\cdot\mathbf{R} \tag{10}$$

then to make further progress we must have recourse to models.

The simplest of these, that of free rotation of the Ga_2 complexes, leads to $F(KR, \mathbf{r}) = j_0(KR)$, with $j_0(x)$ the spherical Bessel function $\sin x/x$. The important property of this model is that $F(KR, \mathbf{r})$ is independent of $\mathbf{r}$, and hence, from eqs. (9) and (10), $\overline{S_{12}(K)} \cong j_0(KR)\, S_{12}(K)$, $S_{12}(K)$ denoting the bond-centre-Ga structure factor. The only information we have on $S_{12}(K)$ which is relevant here is (a) that for two-component hard spheres[7,2] and (b) experimental data for Cu_6Sn_5[4]. Though (b) is obviously not for a small concentration of a larger component Sn, it is nevertheless striking that S_{12} has a pronounced, and narrow, peak at, or very near, the Cu–Cu peak. We stress too that the size differences in Cu–Sn are comparable with those appropriate to Ga_2–Ga†. When we go to the data (a), which is known as a function of concentration, again for small size differences, we find the peak of S_{12}, though less sharp than for Cu–Sn, is again close to the peak in S_{11}, 1 being the smaller component. It is the presence of this peak in $S_{12}(K)$ to which we ascribe the shoulder in $S(K)$ for liquid Ga at 50°C. The factor $j_0(KR)$ multiplying $S_{12}(K)$ will not be reflected in the experiments at all directly, firstly because of the distribution in R which will cause smearing and secondly because the form of $P(\Omega, \mathbf{r})$ in (10) will affect the shape of $F(KR, \mathbf{r})$.

Concerning this latter point, we have also worked out an extreme correlation model in which, to get at $\overline{S_{12}(K)}$, we assumed that, for a given direction of a Ga_2 axis, a free Ga lay along a line through one nucleus of the Ga_2 complex, making an angle α with the Ga_2 axis. We then obtained the result

$$\overline{S_{12}(K)} = \int_{R}^{R\tan\alpha} 4\pi r^2 \left[g_{12}(r) - 1\right]\left[j_0(K|\mathbf{R} - \mathbf{r}|) + j_0(K|\mathbf{R} + \mathbf{r}|)\right]. \qquad (11)$$

This model was suggested by the β-phase of crystalline Ga (from a summary of the facts, see for example reference 1), in which there is a zig-zag chain, the angle α being $\cong 72°$. Though the result is model dependent, it appears that if we introduce a distribution function in angle α with a sufficiently large width, then the result for $\overline{S_{12}(K)}$ will again reflect the structure factor $S_{12}(K)$, the Fourier transform of $g_{12}(r)$ in (11).

But we stress that, in each model, the essential point is to correlate three atoms in a manner transcending a simple central pair potential model. In the limit of sufficiently low temperatures, we anticipate that $S_{12}(K)$ will have to reflect the type of correlations in crystalline phases but our models are presently too primitive on this point.

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†To achieve consistency with thermodynamics, i.e. with the $K = 0$ limit in eqn (6), the Kirkwood–Buff formula for the compressibility of a two-component system requires us to take the volume of Ga_2 to be twice that of G_a.

4 SUMMARY

In summary, the theory of A–B alloys with compound formation embodied in Eqs. (3–5) can be developed approximately for pure Ga metal for sufficiently small concentrations of the assumed Ga_2 complexes. It is argued from available data on two-component systems that it is the peak in the bond-centre –Ga structure factor which is responsible for the shoulder in S(K) observed at 50 °C by Ascarelli[1]. However, and of greater importance, when 3-component hard sphere data becomes available, calculations on an alloy such as Mg–Bi, with Mg_3Bi_2 complexes, will now be possible from the theoretical approach outlined here.†

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†*Note added in proof.* Since this work was completed, a closely related approach has been reported by Bhatia and Ratti (1975, *Physics Letters*, 51A, p. 386).