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## Covalency in liquid Si and liquid transition-metal–Si alloys: x-ray diffraction studies

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**Abstract.** We present data, obtained by x-ray diffraction measurements, of the structure factors for pure liquid Si, and for liquid Ni–Si and Cu–Si alloys. We find it possible to analyse these data as well as data for Fe–Si by decomposition of  $rg(r)$  where  $g(r)$  is the pair distribution function; this analysis provides evidence for Si–Si covalency both in pure liquid Si and in the Si-rich liquid alloys. The degree of covalency in the Si-rich alloys appears to increase with changing species in the order Fe  $\rightarrow$  Ni  $\rightarrow$  Cu.

### 1. Introduction

There has been steady interest for a number of years in the structural and electronic properties of the amorphous and liquid transition-metal–metalloids (TM–B, where B = C, Si, Ge, . . . , e.g. Ni–Si (Waseda and Tamaki 1975) TM<sub>4</sub>B (Bennett *et al* 1971), Mn–Si (Nassif *et al* 1983), Fe–Si Kita *et al* 1982) and Pd–Si (Andonov 1976, Muller *et al* 1978); recently, an unusual degree of theoretical interest in pure liquid Si and Ge has been seen, as new theoretical techniques have been used to address the physical and electronic structure and the degree of covalency that exists in these liquids (Kahl and Hafner 1984, Jank and Hafner 1990, Arnold *et al* 1989, Car and Parrinello 1987, Stich *et al* 1989, 1991). Most experimental studies of the liquid TM–B alloys have focused on the TM-rich region; dilute Si appears to enter the crystalline and amorphous TM structure interstitially (Bennett *et al* 1971), but Si atoms apparently enter the molten TM structure in this concentration range substitutionally (Kita *et al* 1982). In the present study we present and analyse x-ray diffraction measurements of the structures of several liquid TM–Si alloys, with special emphasis on the Si-rich region. In this way we draw these two fields of study together, addressing the question of the extent of covalency that exists in pure liquid Si (and Ge), and the way in which this is altered by the addition of TM atoms to the melt.

### 2. Experimental method

Alloy samples were prepared to premelting mixtures of pure TM and Si in an Ar–10% H<sub>2</sub> atmosphere; nominal purities for the starting material were 99.97% for Ni, 99.999% for Cu and 99.999% for Si.

The x-ray diffraction measurements were carried out on the liquid alloys by a free-surface reflection method using a  $\theta$ – $\theta$  diffractometer (for details, see Kita *et al* 1982). Mo

$K\alpha$  radiation was used, allowing data to be taken from  $Q \sim 1 \text{ \AA}^{-1}$  to  $Q \sim 12 \text{ \AA}^{-1}$ . Multiple scans, resulting in an accumulation of more than  $3 \times 10^4$  counts per angle, reduced the *total* estimate of error for the structure factor,  $A(Q)$ , to less than about  $\pm 2\%$ .

For diffraction measurements, the alloy samples were held in alumina cells, allowing a meniscus area of  $25 \text{ mm} \times 35 \text{ mm}$ , under a purified Ar–10%  $\text{H}_2$  atmosphere. Measurements were taken at  $50^\circ\text{C}$  above the alloy liquidus for each concentration, with the temperature controlled to  $\pm 5^\circ\text{C}$ . The measurement temperature ranges were as follows: for Cu–Si alloys, 1130 (pure Cu) to 1470 (pure Si) with the lowest temperature being 850 at the 30 at.% Si eutectic; for Ni–Si alloys, 1510 (pure Ni) to 1470 (pure Si) with the lowest temperature being 1030 near the eutectic around 50 at.% Ni, where the temperatures are in  $^\circ\text{C}$ . The phase diagrams for these alloys were taken from Massalski (1986).

### 3. Results

The measured structure factors,  $A(Q)$ , for liquid Ni–Si and Cu–Si are shown in figure 1 for concentrations in the Si-rich region. (Our results for pure liquid Ni and Cu (and Fe) agree well with data from Waseda (1980). In particular, the positions of the primary peaks in  $A(Q)$  agree to within  $\pm 0.02 \text{ \AA}^{-1}$ , and those of the second peaks to within  $\pm 0.3 \text{ \AA}^{-1}$ . Moreover, the heights of the primary peaks in  $A(Q)$  agree to within  $\pm 4\%$ , and the positions of the first peaks in  $rg(r)$  agree to better than  $\pm 0.05 \text{ \AA}$ . We do note a small pre-peak in our pure Cu and Cu–Si alloy data that is not seen in our other results or in the literature data for pure Cu. We take this small peak to be an artifact, but of unknown origin. The analysis we present in this report is on the data which include this pre-peak. However, we find that if we remove this pre-peak by extrapolating  $A(Q)$  smoothly to  $Q = 0$ , an analysis of this smoothed  $A(Q)$  provides results that are virtually identical to the results we report. We see, then, that the existence of this small pre-peak does not appear to weaken our analysis or results. We note again that in all other respects our data agree very well with literature values.) We have also measured  $A(Q)$  for the TM–Si alloys in the TM-rich region, but can detect no measurable change in  $A(Q)$  from the pure liquid TM data up to about 30–50 at.% Si. We therefore do not reproduce the results for the TM-rich region here. While measurements on liquid Fe–Si were not a part of the present study, we do analyse data reported earlier for this system (Kita *et al* 1982) applying our analysis to the Si-rich regime of this alloy via the techniques we will describe. It is immediately evident from figure 1 that the main peak in  $A(Q)$  for pure liquid Si is really a double peak, and that the main peak in the alloys also remains low in intensity and asymmetric in shape. The iterative smoothing procedure of Kaplow *et al* (1965) has been used in this analysis. (Our results for pure liquid Si agree well with data that have been published earlier: see, e.g. Waseda (1980), Gabathuler and Steeb (1979) and Waseda and Tamaki (1975).) It is the physical significance of this asymmetry that we pursue in this report.

### 4. Analysis and discussion

Structural information is usually extracted from the measured  $A(Q)$  for various materials by examination of  $g(r)$ , the pair distribution function, which is obtained as a Fourier transform of  $A(Q)$ . Furthermore, the radial distribution function,  $R(r)$ , given by

$$R(r) = 4\pi n_0 r^2 g(r) \quad (1)$$

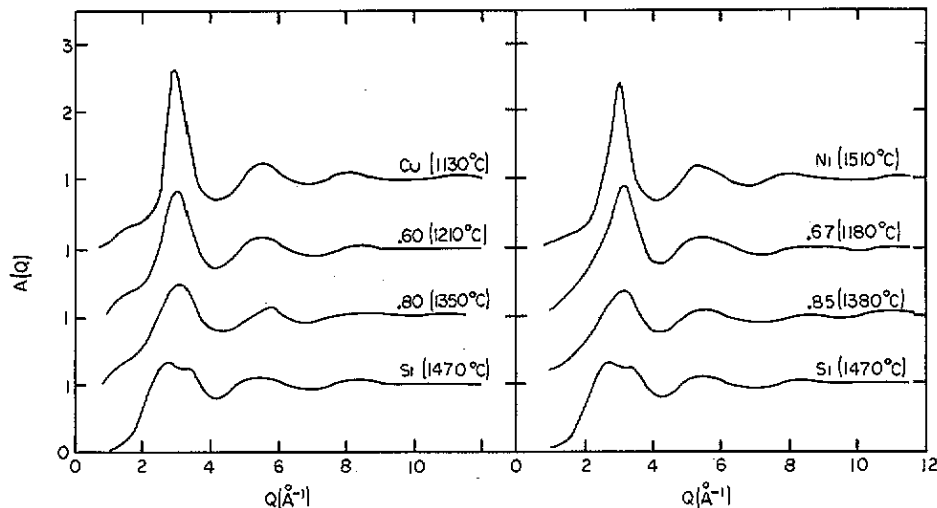


Figure 1. The measured x-ray structure factors,  $A(Q)$ , for liquid Cu-Si and Ni-Si alloys, as well as for pure liquid Cu, Ni and Si are shown. Measurements were made at 50°C above the liquidus. Atomic fractions of Si for the alloys are indicated on the figure.

can be integrated to yield coordination numbers  $n_c$ , for various peaks in  $R$ . (Here  $n_0$  is the mean atomic number density for the liquid.)

An analytical technique that is commonly used for the analysis of the structures of glasses and molecular solids involves decomposition of  $g(r)$ , and subsequent identification of the separated peaks according to the alloy species pair ( $i, j$ ) that contributes to it. This technique has been difficult to apply successfully to liquid alloys, since the decomposed peaks tend to be broader, are more likely to overlap substantially and are more difficult to identify in terms of the alloy components contributing to them. The Si-rich TM-Si liquid alloys, however, appear to be an exception to this, allowing meaningful analysis via this technique. This is due in large part to the fact that the second peaks in  $g(r)$  for liquid Si and the liquid TMs are rather clearly separated. In particular, whereas the positions  $r_1$  of the first peaks for liquid Si and the liquid TMs are virtually indistinguishable, the ratio  $r_2/r_1$  (the ratio of the position of the second peak to that of the first) is about 1.9 for the liquid TMs (as it is for most liquid metals), but is only about 1.5 for pure liquid Si (and Ge). Thus the second peaks in  $g(r)$  for the TMs and for Si are well separated in  $r$ , and can be readily distinguished. We will therefore use this technique to analyse the structures of both pure liquid Si (and Ge), and the Si-rich TM-Si liquid alloys. It should be emphasized, however, that even though we can identify the decomposed peaks rather well, they are still broad and overlap one another substantially. As a result, our analysis should be seen as being indicative of covalency and not highly quantitative. Care has been taken to provide estimates of uncertainty throughout. (Andonov (1976) used a similar method, decomposing  $r^2g(r)$  for liquid  $\text{Pd}_{0.825}\text{Si}_{0.175}$  in the region of the second peak in  $g(r)$  to obtain estimates of coordination numbers for Pd and Si in this Si-dilute alloy. We apply our analysis to the Si-rich region of our TM-Si alloys.)

Because our analysis of the structure of the liquid TM-Si alloys depends critically on an understanding of the structure of pure liquid Si, we begin with a discussion of this liquid. Moreover, because of the strong similarity of liquid Ge to liquid Si, and because of the active current interest in both of these liquids (Kahl and Hafner 1984, Jank and Hafner

1990, Arnold *et al* 1989), we will also briefly include information on Ge as we discuss Si. (To be able to discuss pure liquid Si and Ge on an equal footing, we will use the diffraction data for both as published by Waseda (1980) in addition to our data for liquid Si. Our results for Si are very close to those of Waseda, and we have none for Ge.)

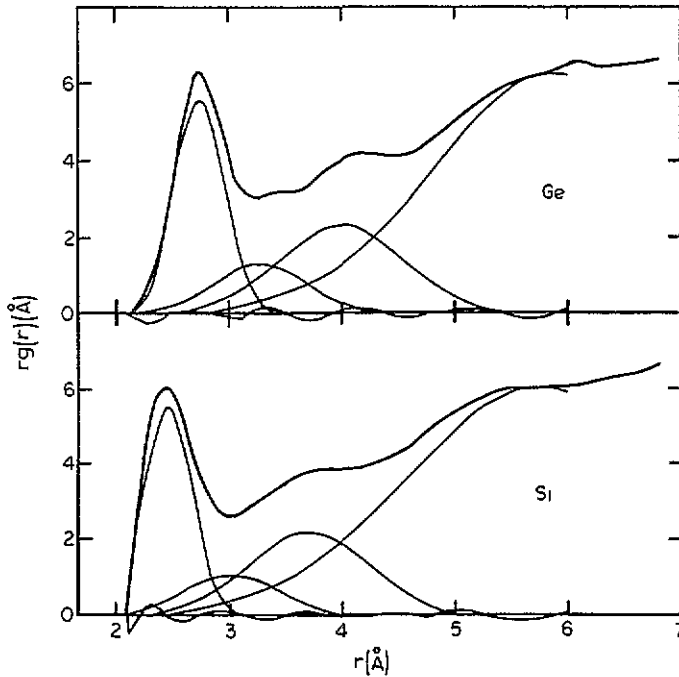


Figure 2. A four-peak decomposition of  $rg(r)$  for pure liquid Si and Ge. Data for both are from Waseda (1980). The quality of the decomposition can be seen in the total difference curve, which oscillates about zero.

Table 1. Results of the analysis, by decomposition, of  $rg(r)$  for pure liquid Si and Ge. (w indicates data from Waseda (1980) and p, present data).

Element	$n_0$ ( $\text{\AA}^{-3}$ )	$r_1$ ( $\text{\AA}$ )	$n_c(1)$	$(8/3)^{1/2}r_1$ ( $\text{\AA}$ )	$r_2$ ( $\text{\AA}$ )	$n_c(2)$	$r_2/r_1$
Si (w)	$5.551 \times 10^{-2}$	2.46	5.8	4.02	3.70	8.4	1.50
Si (p)	$5.551 \times 10^{-2}$	2.50	4.8	4.08	3.88	10.8	1.55
Ge	$4.611 \times 10^{-2}$	2.73	6.1	4.46	3.99	8.5	1.46

The results of a four-peak decomposition of  $rg(r)$  for pure liquid Si and Ge are shown in figure 2. We have chosen to decompose  $rg(r)$  rather than  $g(r)$  or  $r^2g(r)$  since, at least on a quasicrystalline model, shells in  $rg(r)$  are expected to be symmetric (Coulson and Rushbrooke 1939). A Gaussian form is assumed for each shell, and all the parameters (three per peak: position, width and height) are adjusted via a least-squares fitting routine. The substantial similarities between the structures of liquid Si and Ge are immediately evident, and the fit can be seen to be quite good. Parameters resulting from our analysis,

shown in table 1, highlight these similarities. (It can be seen that the results of the analysis of our data for liquid Si closely resemble those obtained from the data of Waseda (1980). Further comment will be made on this below.) Several of these parameters are worthy of emphasis. In particular, the coordination numbers,  $n_c(1)$ , of the first peak in  $g(r)$  are 5.8 (Si) and 6.1 (Ge). These are a little below mean values found in the literature: 6.4 (Si) and 6.5–7.1 (Ge) (Waseda 1980, Gabathuler and Steeb 1979, Bellissent-Funel and Bellissent 1984, Isherwood *et al* 1972). (We will discuss the way in which we obtained these  $n_c(1)$  below.) Likewise,  $n_c(2)$  is found to be about 8.5 for each of these liquids. If our samples were composed entirely of rigid covalently bonded tetrahedral units, we would expect only four nearest neighbours,  $n_c(1)$ , at  $r_1$ , and several (about 12) next-nearest neighbours,  $n_c(2)$ , at  $r_2 = (8/3)^{1/2}r_1$ . This situation is closely approximated in both crystalline and amorphous Si and Ge. Also, a tetrahedral bond angle,  $\alpha$ , of  $109.5^\circ$  would be expected. This is also very nearly true for both crystalline and amorphous Si and Ge, although a bond angle variation,  $\Delta\alpha$ , of about  $\pm 10^\circ$  is predicted and observed for the amorphous phase (Temkin *et al* 1973). We see from table 1 that our positions for  $r_2$  fall 4% (Si (P)), 8% (Si (W)) and 11% (Ge) below the values  $(8/3)^{1/2}r_1$  expected for a rigid tetrahedral structure. Moreover, the  $n_c(2)$  we obtain are rather too small. We interpret this in the following way. The remarkably open structure indicated by the low values of  $n_c(1)$  indicates a substantial degree of covalent bonding that has survived into the liquid. It is likely that these bonds are not permanent, however, but rather that they form and dissipate, allowing a somewhat more relaxed (relaxed toward a more closely packed arrangement) liquid structure to form. This results in a value of  $n_c(1)$  above the value of four and a value of  $n_c(2)$  below  $\sim 12$  expected for a rigid open tetrahedral structure. If we assume that atoms are at  $r_2$  because of the existence of covalent bonds (as in the rigid structure), we may use our measured  $r_2/r_1$  to estimate the bond angle  $\alpha$  in these liquids; the result is  $\alpha(\text{Si (W)}) = 98^\circ$ ,  $\alpha(\text{Si (P)}) = 103^\circ$  and  $\alpha(\text{Ge(W)}) = 94^\circ$ . Even though the decomposed peak centred at  $r_2$  is very broad in each case (as is the equivalent distribution calculated by Stich *et al* (1989, 1991) — see comments below), the central value,  $r_2$ , quite clearly places  $\alpha$  substantially below the value of  $109.5^\circ$ , indicating a partial relaxation of the liquid structure toward a more close-packed arrangement.

Certain differences between our data for liquid Si and those of Waseda are worthy of comment (see table 1.) In particular, we note that our data show a lower value for  $n_c(1)$  and a higher value for  $n_c(2)$  than do Waseda's data, placing ours closer to what one would expect for an ideal rigid tetrahedral structure. Moreover, our higher estimate of the bond angle ( $\alpha = 103^\circ$ ) is also consistent with this. We suspect that, even though our data and Waseda's were measured at nominally the same temperature, some differences in the thermal history of the samples may have resulted in a slightly different liquid structure. (It is generally noted that the melting of pure Si and Ge is not a simple process, but one that is rather time and temperature dependent. For example, Glazov *et al* (1969) note that Si and Ge 'melt very slowly' at temperatures close to the melting point. They held their samples  $15\text{--}20^\circ\text{C}$  above the melting temperature,  $T_m$ , for 4–5 h to ensure melting, and attribute this slow melting to a high heat of fusion. Waseda and Suzuki (1975) heated their Si and Ge samples to  $100^\circ\text{C}$  above  $T_m$  to ensure melting, then lowered the temperature to the desired value for their x-ray diffraction measurements. Moreover, Bergman *et al* (1985) mention an 'unexplained' time dependence of their measured neutron scattering intensity for liquid GaAs, a liquid that shows strong structural similarities to liquid Ge and Si. We suggest that, in each case, these time- and temperature-dependent effects are due to the progressive breaking of covalent bonds just above  $T_m$ . In no case did we hold our samples above the measurement temperature ( $T_m + 50^\circ\text{C}$ ) for an appreciable period of time.) We do not consider the difference in  $r_2$  between our data for pure Si and Waseda's ( $\sim 3.7 \text{ \AA}$  versus

$\sim 3.9 \text{ \AA}$ ) to be significant for the interpretation of our liquid alloy structures; we take the value  $r_2 = 3.70 \text{ \AA}$  for this analysis.

Gabathuler and Steeb (1979) and Gabathuler *et al* (1979) have analysed their neutron diffraction measurements on liquid Si, Ge and Al-Si alloys in a somewhat different way. They assume the existence of some fraction of ideal rigid tetrahedral units of Si or Ge atoms in melts of otherwise free atoms, and then estimate the fraction of the atoms in these tetrahedra by fitting the measured structure factors to those calculated on the basis of this mixture of free and bound atoms. In this way they estimate that about 75% of Ge atoms and 63% of Si atoms are bound into tetrahedra in these pure liquids. It is satisfying that their estimates of covalency are similar to ours, (we estimate on the basis of our  $n_c$  values that  $\gtrsim 70\%$  of the atoms experience covalent bonding in both liquid Si and Ge), but in our analysis we are also able to estimate the degree of relaxation of the tetrahedral unit, as seen in the reduced value of  $\alpha$  below  $109.5^\circ$ .

Some recent calculations seem to support this interpretation. Jank and Hafner (1990) simulate the atomic structures of these pure liquids via a molecular dynamics (MD) calculation and obtain the electronic structure self-consistently from a super-cell calculation based on linear muffin-tin orbitals; Stich *et al* (1989, 1991) report the results of an *ab initio* approach that combines an MD calculation with an accurate local density approximation. Stich *et al* show the formation of weak covalent bonds on about 25–30% of the atoms in metallic liquid Si and Ge, and via a contour plot of valence electron density versus time are able to observe the formation and dissipation of these unstable bonds on a time scale of about  $10^{-13}$  s. Moreover, both calculations show a broad overall distribution of bond angles with a peak somewhat below the ideal value of  $109.5^\circ$ . (Stich *et al* find, in addition to a narrow peak at  $\sim 60^\circ$ , a broad peak giving  $\alpha \cong 100^\circ$  for liquid Si, rather close to our experimental value.) We therefore find a satisfying degree of consistency between our analysis of  $g(r)$  and these recent calculations. We therefore will interpret the peak at  $r_2$  in liquid Si and Ge as being an Si-Si (or Ge-Ge) peak, indicative of the existence and extent of covalency in these liquids, and will also consider  $r_2 = 3.70 \text{ \AA}$  as the position of the Si-Si peak in the liquid TM-Si alloys, interpreting our alloy data accordingly.

We have so far said nothing about the small peak at  $r' = 3.01 \text{ \AA}$  (Si) and  $r' = 3.28 \text{ \AA}$  (Ge). These small peaks are found to occur as a result of the decomposition of each of the several pure liquid metals and alloys we examined, including the pure liquid TMs, always of nearly the same relative size and in the same relative position. It appears that this small peak reflects the degree to which a Gaussian shape imperfectly fits the 'wings' of the first two peaks in  $rg(r)$ ; this is therefore an 'error peak' that straddles the first minimum in  $g(r)$ , but has little influence on the positions  $r_1$  or  $r_2$ . (We note that there is no consensus in the literature on the form that should be assumed for the first peak in  $g(r)$ , and, consequently, on how  $n_c(1)$  should be obtained. The existence of this 'error peak' indicates that we also have no conclusive answer to this. We also note that a rather wide range of values is obtained for  $n_c(1)$ , depending upon which of several standard methods one uses to parametrize this first peak. As an example, one obtains, using data for  $g(r)$  for liquid Ni at  $1500^\circ\text{C}$  from Waseda (1980), values for  $n_c(1)$  ranging from 8.7 (assuming a symmetric  $rg(r)$  for this peak) to 11.6 (integrating the  $R(r)$  to the first minimum), with other methods giving intermediate values. Waseda (1980) observes a similar spread in values for  $n_c(1)$  for the liquid noble metals in his analysis.) In calculating  $n_c(1)$  and  $n_c(2)$  for these liquids we have therefore assigned half of the coordination number for this small peak to each of  $n_c(1)$  and  $n_c(2)$ , thereby increasing each of these by approximately one. We therefore estimate our uncertainties for  $n_c(1)$  and  $n_c(2)$  to be about  $\pm 0.7$ . These uncertainties are not really larger, however, than should apparently be assigned to other values presently in the literature. Moreover, because

we use one method throughout to calculate  $n_c(i)$ , the relative changes we observe should carry less uncertainty than do the absolute values of these parameters.

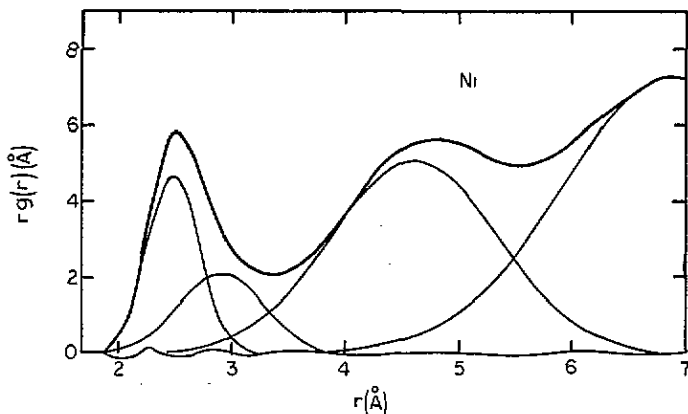


Figure 3. A four-peak decomposition of  $r_g(r)$  for pure liquid Ni, with data taken from our present measurements. The total difference curve can be seen oscillating closely about zero, indicating a high-quality fit.

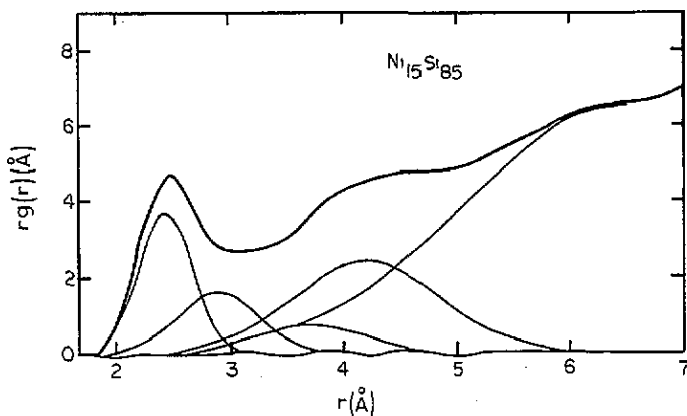


Figure 4. A five-peak decomposition of  $r_g(r)$  for the liquid alloy  $\text{Ni}_{15}\text{Si}_{85}$ . One peak is fixed in position at  $r = 3.70 \text{ \AA}$ , but all 14 other fitting parameters are allowed to vary. The total difference curve is again displayed.

To proceed with the analysis of the liquid Si-rich TM-Si alloys, we first decompose  $r_g(r)$  for pure liquid Fe, Ni and Cu, using a four-peak decomposition routine with all parameters allowed to vary. The results for all three liquids are similar; we show the result for liquid Ni in figure 3. Again the fit is excellent. In each case,  $r_1$  falls very close to  $2.50 \text{ \AA}$ , and  $r_2$  falls at about  $4.60 \text{ \AA}$ . We also note that there is no peak near  $3.7 \text{ \AA}$ , the position at which we would look for an Si-Si peak indicating covalency in the liquid alloy. The decomposition of the  $r_g(r)$  for the Si-rich alloys is then performed with a five-peak



fitting routine, with the position of one peak fixed (in position only) at 3.7 Å and with all the 14 other parameters on the five peaks free to take on optimal values. This allows us to test specifically for the existence of the Si-Si covalency peak, since its height and width will then directly reflect the degree to which the Si-Si covalent bond is populated. An example of this analysis is shown for liquid Ni<sub>15</sub>Si<sub>85</sub> in figure 4. The results for other alloys are similar. In each alloy we note a peak within  $\leq 8\%$  of 4.60 Å; we interpret this as a TM-TM peak, as seen in the analysis of the  $g(r)$  for the pure TM (see figure 3). Varying evidence for a peak at 3.7 Å is also seen in these alloys. Interpreting this as an Si-Si peak, we calculate the corresponding coordination numbers and display these as a function of Si concentration in figure 5. (In each case we have used the approximate method of Andonov (1976) to estimate the relative scattering strengths of the TM and Si atoms for x-rays, and to calculate the appropriate coordination numbers.) It should be noted that the relative uncertainty in  $n_c(\text{Si-Si})$  as shown in figure 5 is rather large for points for  $c(\text{Si}) < 0.7$  (representative uncertainties are shown), since the scattering factor for Si becomes quite small in this region relative to that for the alloy. From the figure it appears that a certain degree of covalency does exist in the liquid TM-Si alloys, for  $c(\text{Si}) > 0.9$  for Fe-Si,  $c(\text{Si}) > 0.7$  for Ni-Si and  $c(\text{Si}) > 0.6$  for Cu-Si. Moreover, the fraction of the Si atoms that are involved in covalent bonding in Si-rich TM-Si alloys appears to increase in the order of TM solutes Fe  $\rightarrow$  Ni  $\rightarrow$  Cu.

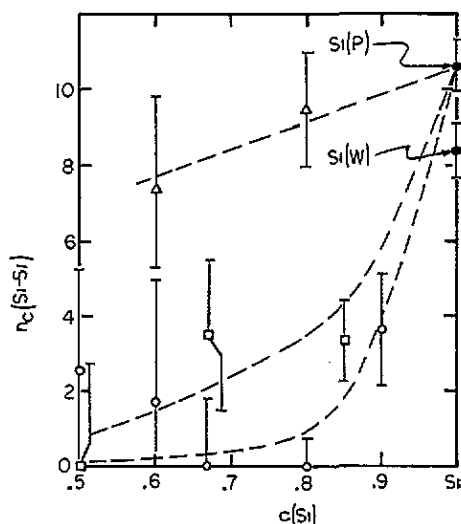


Figure 5. The coordination number,  $n_c(\text{Si-Si})$ , of the decomposed peak at  $r = 3.70$  Å as a function of  $c(\text{Si})$  for liquid Fe-Si (O), Ni-Si (□) and Cu-Si (Δ) alloys.

The results of measurements by Waseda and Tamaki (1975) are also consistent with our results. They used anomalous x-ray scattering to obtain estimates of the partial structure factors for liquid Ni-Si alloys. They found that the Si-Si partial structure factor for the alloys is similar to that for pure liquid Si. We interpret this to mean that covalent Si-Si bonds exist in the alloys as in the pure liquid.

We attempt one final test of our analysis: we have assumed that the peak at  $r \sim 4.6$  Å in  $rg(r)$  for each of our TM-Si alloys is due to TM-TM coordination. We therefore expect the coordination number for this peak,  $n_c(\text{TM-TM})$ , to approach zero continuously as  $c(\text{Si})$

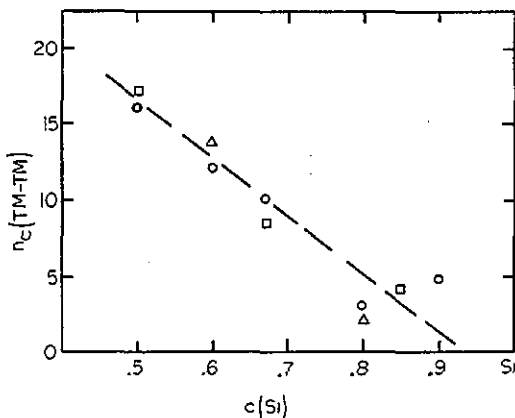


Figure 6. The coordination number,  $n_c(\text{TM-TM})$ , of the decomposed peak at about 4.6 Å as a function of  $c(\text{Si})$  for liquid Fe-Si (○), Ni-Si (□) and Cu-Si (△) alloys.

approaches unity. These  $n_c(\text{TM-TM})$  have been calculated, and are presented in figure 6; they do indeed approach zero continuously as expected.

## 5. Conclusions

We find that it is possible to analyse meaningfully the structure of liquid Si and Ge, and of liquid TM-Si alloys in the Si-rich region, by decomposition of  $rg(r)$  for these liquids; this analysis provides evidence that some degree of Si-Si covalency exists in these alloys, as it does in pure liquid Si (and Ge). Moreover, the degree of covalency in the alloys appears to increase with changing TM species in the order Fe → Ni → Cu.

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