Atomic ordering in liquid Si and Ge by structural diffusion model calculations

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Abstract. A semi-empirical model for the atomic-scale structure of liquid Si and Ge has been constructed on the basis of atomic arrangements with the structure of the normal and high-pressure phases of solid Si and Ge. It has been found that liquid Si and Ge have quite similar atomic orderings, exhibiting the local tetrahedral features of the considered solid phases of Si and Ge where the features of the high-pressure phase predominate over those of the normal phase. The present model picture has been found to account well for the peculiar character of the solid–liquid phase transition in Si and Ge.

1. Introduction

Liquid Si (l-Si) and liquid Ge (l-Ge) are known to exhibit peculiar structural features which cannot be reproduced by the random-hard-spheres packing type of model commonly invoked to describe the atomic arrangement of liquid metals. The features are as follows [1].

(i) The first peak in the static structure factors $S(q)$ for l-Si and l-Ge has a very pronounced shoulder on the higher side of the wavevector q.

(ii) The atomic pair distribution function $g(r)$ for l-Si and l-Ge shows no deep minimum between the first and the second main peaks; instead, a flat maximum is located in this region.

(iii) The number of first atomic neighbours in l-Si and l-Ge is approximately six which is lower than the 10–11 nearest atomic neighbours found in most liquid metals.

These peculiar features are assumed to originate from the fact that a fraction with the nature of the crystalline state of Si and Ge survives in their liquid state [1, 2].

Recently, we verified this assumption by constructing and carefully analysing three-dimensional reverse Monte Carlo models of l-Si and l-Ge which completely reproduce their essential structural features [3]. Clear signatures of local tetrahedral atomic ordering in both liquid metals have been found, which indicate that the atomic-scale structure of l-Si and l-Ge does retain some memory of the structures of solid Si and Ge, which is also of the tetrahedral type [4]. Further detailed analyses of the geometrical characteristics of the model structures showed that, in fact, the atomic arrangement in l-Si and l-Ge is not very close to that of normal form of solid Si and Ge, which has a diamond-type structure and semiconductor properties, but resembles that of the high-pressure modification of solid Si and Ge, having the white-tin-type structure and metallic conductivity. Fragments of both types of crystalline structure, illustrating their inherent tetrahedrality and close relationship, are given in figure 1. On the basis of this result we suggest that, on melting, the regular atomic structure of solid Si and Ge is not completely destroyed and randomized, but most probably due to the strong directed bonding between the constituent atoms it collapses from
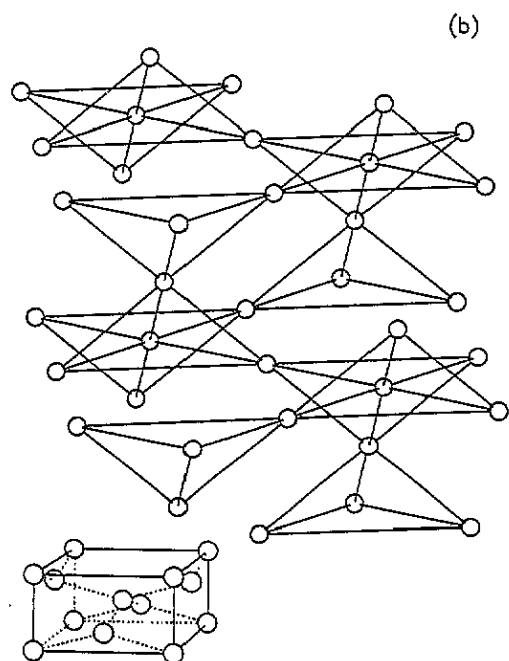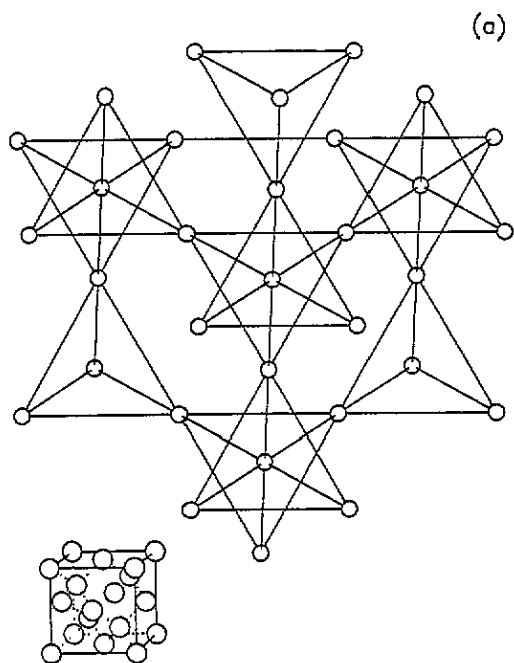
Figure 1. Fragments of the crystalline lattices of (a) the normal form of solid Si and Ge with the diamond-type structure and (b) the high-pressure modification of solid Si and Ge with the white-tin-type structure. The unit cells of both lattices are given in the lower parts of the figures. For legibility, the crystalline fragments and the corresponding unit cells are not on the same scale.

the diamond-type structure towards the more densely packed white-tin-type arrangement, preserving the local tetrahedrality. This model picture explains well the persistence of the tetrahedral features of the solid Si and Ge structure in the l-Si and l-Ge structures. It also complies with the anomalous increase in the density and the change in the type of conductivity observed on melting Si and Ge [5]. It is thus to be expected that, by considering the diamond-type structure as a parent atomic arrangement and the white-tin-type structure as a offspring atomic arrangement resulting from the melting process, it should be possible to construct a structure model that incorporates their common tetrahedral features and describes well the atomic ordering in l-Si and l-Ge. In the present work this expectation is checked out by carrying out structural diffusion model calculations for both crystalline structures under consideration.
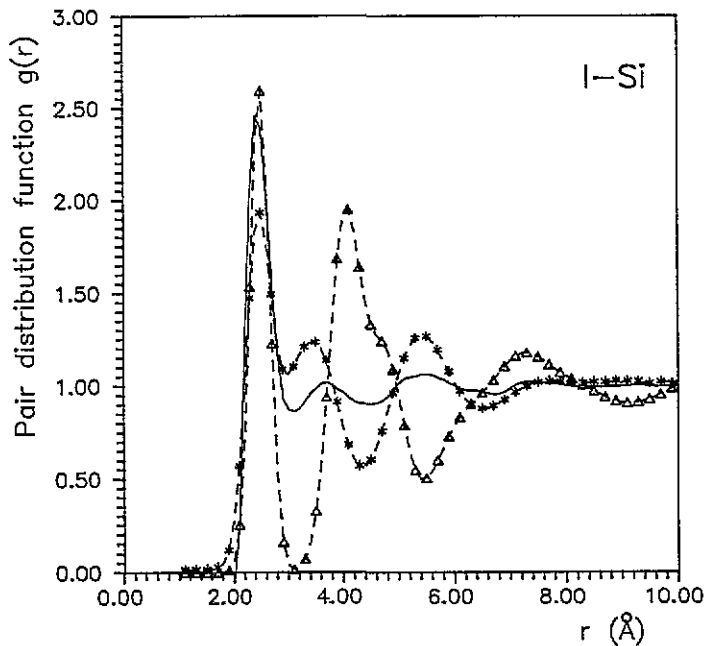

Figure 2. Comparison between the model PDFs for Si with the liquefied diamond-type atomic arrangement (----△----) and liquefied white-tin-type atomic arrangement (----*----) and the experimental PDF for liquid Si (——).

2. Structural diffusion model calculations for liquid Si and Ge

The structural diffusion modelling method consists of destroying the long-range spatial order in the perfect crystal considered, i.e. liquefying the crystal structure, by substituting the δ peaks of its pair distribution function (PDF) for Gaussian distributions the widths of which increase with increase in interatomic distances, and a subsequent search for agreement between the thus calculated PDF and the experimental value. The presence of such agreement would indicate that the local atomic arrangements in both the disordered system and the tested crystal exhibit similar features and, consequently, both are built
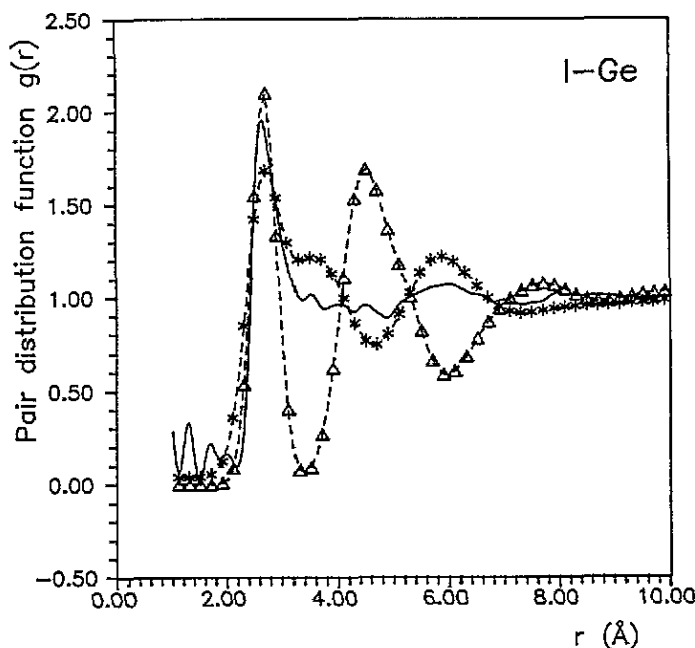
Figure 3. Comparison between the model PDFs for Ge with the liquefied diamond-type atomic arrangement ($----\triangle----$) and liquefied white-tin-type atomic arrangement ($----*----$) and the experimental PDF for liquid Ge (———).

of similar structural units arranged in identical coupling schemes. The method has been successfully applied for selecting structure models for both liquid [6] and solid [7,8] disordered materials. Thus the calculated model PDFs for the liquefied diamond-type and white-tin-type arrangements of Si and Ge atoms are shown in figures 2 and 3, respectively, together with the corresponding experimental PDFs for l-Si and l-Ge obtained by x-ray diffraction experiments [1,9]. The calculations were carried out with the respective data for the considered crystal structures of Si and Ge all taken from literature sources [10–12]. In order to account for the thermal expansion of the interatomic distances accompanying the melting process of Si and Ge the r-scale data of all model PDFs were multiplied by appropriate factors not exceeding 1.05. The values for the multiplicative factors were empirically selected so that the first peaks in the model PDFs agreed with the position of the first peak in the respective experimental PDFs. A similar r-scaling procedure has been frequently applied to obtain better agreement between model and experimental PDFs [8]. Model PDFs have been calculated, and comparison with the experimental PDFs for l-Si and l-Ge has been carried out up to interatomic distances of only 10 Å, since there are no important structural features in the experimental data above this real-space distance (see figures 2 and 3). As one can see in figures 2 and 3 the model PDFs for the liquefied diamond-type arrangements of Si and Ge atoms, except in the region of the first peak, do not agree with the corresponding experimental PDFs for l-Si and l-Ge. This disagreement shows that no good model for the atomic arrangement in l-Si and l-Ge could be constructed alone on the basis of the structure of the normal forms of solid Si and Ge. The same figures show that there is an approximate correspondence between the shapes of the model PDFs for the liquefied white-tin-type arrangements of Si and Ge atoms, and the respective

experimental PDFs. The correspondence indicates that the structure of the high-pressure modifications of solid Si and Ge could serve as an approximate model for the atomic arrangement in l-Si and l-Ge. These observations correlate well with the results of our previous studies on the structure of l-Si and l-Ge [3,9]. Careful inspection of figures 2 and 3 also shows that the model PDFs for the liquefied diamond-type and white-tin-type arrangements oscillate out of phase in the region above their first peak in such a specific way that a properly constructed superposition of both functions could match the experimental PDFs for l-Si and l-Ge much better than the individual model PDFs do. As one may see in figure 4, composite PDFs obtained by superimposing the model PDFs for the liquefied diamond-type and white-tin-type arrangements, multiplied by weighting factors of 0.2 and 0.8, respectively, agree well with the experimental PDFs for l-Si and l-Ge. It is to be noted that the physical relevance of the thus mathematically constructed composite PDFs is grounded on the suggestions of Wagner and Halder [13] that the total PDF may be expressed in terms of weighted contributions of separate PDFs accounting for all distinct types of atomic arrangement in the disordered system under study. In the present model, two separate atomic distribution functions, one for the liquefied diamond-type arrangement and another for the liquefied white-tin-type atomic arrangement, are considered mainly to contribute to the experimental PDFs of l-Si and l-Ge. Since l-Si and l-Ge are not molecular liquids and, therefore, are not expected to sustain rigid atomic groupings, it is also assumed that the two types of tetrahedral atomic arrangement considered are not at all rigid and, hence, not so well pronounced interactions between them are present and can be accounted for by a third separate PDF. It may be added that structure models involving two distinct types of atomic arrangement only (i.e. two separate PDFs of $S(q)$-values only) have been found fruitful for describing the essential structural features of a number of other single-component liquids such as Hg, Ga, Sn, Bi and Te as well [14, 15]. Structure models for l-Si and l-Ge based on two substructures substantially different from those suggested in the present study have also been put forward [16–18].

3. Discussion

As one may see in figure 4 the composite PDFs reproduce quite well all details of the experimental PDFs for l-Si and l-Ge, including the flat maximum at approximately 4 Å. The model structure factors given in figure 5, obtained by back Fourier transforming the composite model PDFs, also reproduce the experimental structure factors for l-Si and l-Ge well, including the characteristic shoulder on the higher-q side of their first peak. The observed similarities coupled with the fact that the nearest atomic coordinations in l-Si and l-Ge have a rather short lifetime, which according to Enderby and Barnes [19] is indicated by the significant values of the experimental PDFs in the region between their first two main peaks where no deep minimum occurs, suggest that the liquid state structure of Si and Ge may well be described as a convolute of instantaneous local atomic configurations of white-tin-type-like and diamond-type-like tetrahedral orderings with the characteristic features of the former ordering predominating over those of the latter. It is to be noted that the present model picture is quite in line with the findings of other theoretical studies which also predict the presence of local atomic configurations of transient tetrahedral nature in l-Si and l-Ge [20, 21].

It may also be noted that the agreement between the model and experimental structure-sensitive functions for l-Si and l-Ge achieved by the present diffusion model calculations (see figures 4 and 5) is somewhat worse than achieved by our recent reverse Monte Carlo
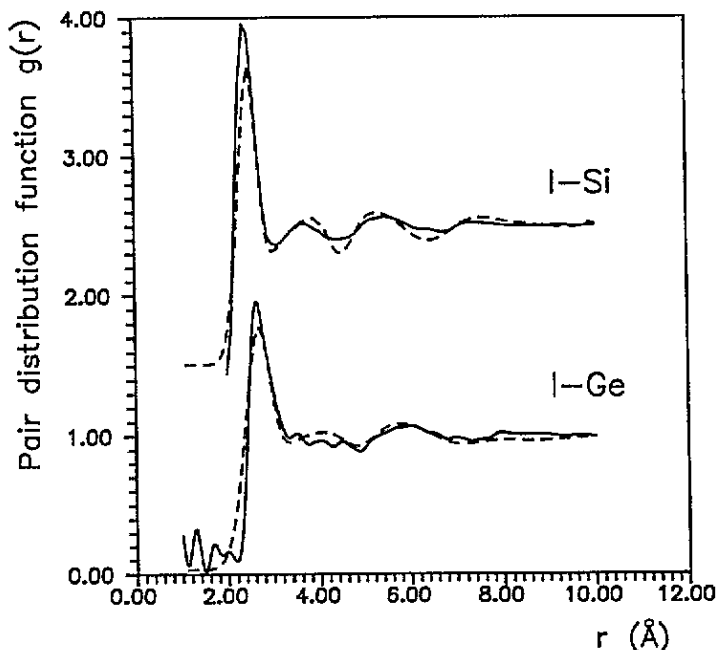
Figure 4. Comparison between the experimental PDFs for l-Si and l-Ge (——) and the model composite PDFs (– – –) incorporating the features of liquefied diamond-type and white-tin-type arrangements of Si and Ge atoms, respectively.

simulations of the structure of l-Si and l-Ge (see figures 1 and 2 in [3]). This is to be expected since no attempt to fit the experimental data by adjusting the parameters of the tested crystalline arrangements has been made. The importance of the present results consists of the fact that, by starting from regular atomic arrangements occurring with solid Si and Ge and not destroying their topological features, we arrived at a model picture for the structure of l-Si and l-Ge which is quite consistent with that resulting from the completely stochastic reverse Monte Carlo simulations; the picture is that the local atomic arrangements of l-Si and l-Ge are rather close to each other and both exhibit local tetrahedral features. Moreover, the results of the present model calculations suggest that a variety of almost perfect (diamond type like; see figure 1) and heavily deformed (white tin type like; see figure 1) tetrahedra of Si and Ge atoms should be present in l-Si and l-Ge, respectively, which may explain why the bond angles between the immediate atomic neighbours in l-Si and l-Ge are found to be so broadly distributed around the perfect tetrahedral angle of approximately 109° (see figure 2 in [13] and figure 6 in [3]).

4. Conclusion

In conclusion, a reasonable model for the atomic-scale structure of l-Si and l-Ge has been constructed on the basis of crystalline arrangements with the structure of solid phases of Si and Ge. The model unambiguously shows that l-Si and l-Ge have quite similar local atomic arrangements showing the tetrahedral features of these phases. In particular, this arrangement is related mainly to that occurring with the high-pressure modification of solid
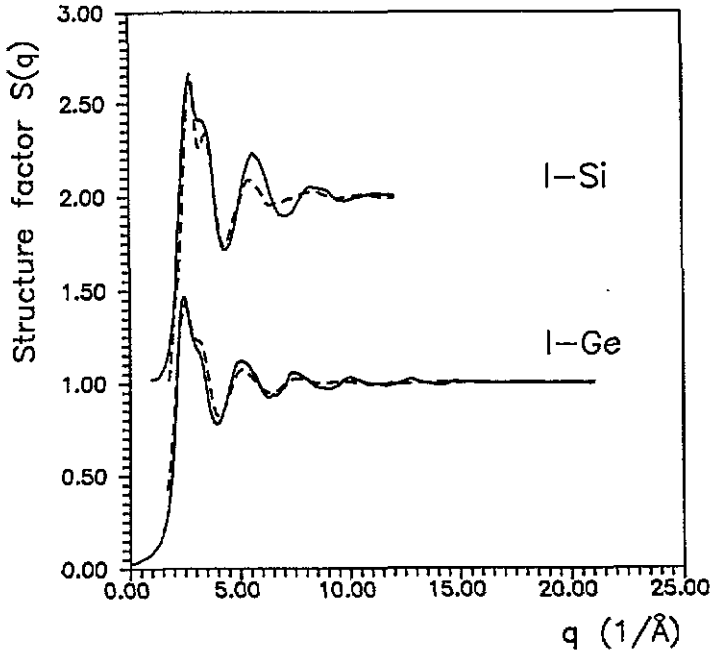
Figure 5. Comparison between the experimental structure factors $S(q)$ for l-Si and l-Ge (———) and the model structure factors (- - -) calculated from the model composite PDFs in figure 4.

Si and Ge and, to a much lesser but not negligible extent, to that found in the normal forms of solid Si and Ge. Thus it has been demonstrated that the melting process of Si and Ge could be considered as a specific spatial rearrangement of the diamond-type ordered Si and Ge atoms towards the white-tin-type-like structure. On crystallization of l-Si and l-Ge the opposite structural transformation should take place. Clusters of the regular diamond-type arrangement, weak traces of which persist in the melt, should easily develop and grow further from the melt at the expense of the dominating continuum of atoms with a white-tin-type-like arrangement. This type of clustering is quite probably responsible for the experimentally observed pre-crystallization anomalies in the structure-sensitive properties of Si and Ge [5].

Acknowledgments

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