

# A Model of the Structure of Liquid Germanium

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A model of liquid germanium is proposed based on two near neighbour distances. The observed interference function at 1047 °C is reproduced, within experimental error, by the superposition of only two different partial interference functions which are approximated by hard sphere interference functions of packing density 0.41 and diameters 2.07 and 2.70 Å.

## 1. Introduction

An earlier paper<sup>1</sup> gave the x-ray interference function for liquid germanium,  $I_{\text{Ge}}(K)$ , [ $K = (4\pi \sin \theta)/\lambda$ ,  $2\theta$  = scattering angle,  $\lambda$  = x-ray wave length] at 1047 °C. The main features (see Fig. 2) were in good agreement with those obtained by earlier workers<sup>2,3</sup> and, in particular, all patterns had a shoulder on the high  $K$  side of the first main peak. This  $I_{\text{Ge}}(K)$  is, therefore, very different from many experimental  $I(K)$  obtained for other liquid metals which do not show this shoulder. In fact, a large number of elemental liquid metals give interference functions which agree very closely with those obtained from a Percus-Yevick hard sphere model<sup>4</sup>. The hard sphere interference function,  $I(K, \sigma, \eta)$  may be calculated for different values of the hard sphere diameter,  $\sigma$ , and packing density,  $\eta$ , and good agreement has been found for  $I(K, \sigma)$  with  $\eta = 0.45$  (e.g. Na, K<sup>4</sup>, Cu, Ag<sup>5</sup> and Hg<sup>6</sup>). This is not true for  $I_{\text{Ge}}(K)$ , as can be seen from Figure 2 on which is plotted  $I(K, \sigma)$  for  $\eta = 0.45$ . The differences between the two curves are largest in the region of the first main peak and are very much larger than the experimental error assigned to  $I_{\text{Ge}}(K)$ <sup>7</sup>. It is clear that all peaks of  $I_{\text{Ge}}(K)$  are smaller and broader than those of  $I(K, \sigma)$ , this fact, together with the presence of the shoulder on the high  $K$  side of the first main peak suggests that the experimental interference function could be looked upon as the superposition of interference functions. It was the object of the present work to find a model from which an interference function could be calculated, which agreed with  $I_{\text{Ge}}(K)$ , and was a combination of simpler, possibly hard sphere, interference functions. To show how this model was obtained it is necessary to refer to the real space model that was used in the previous work<sup>1</sup>. In this work the atomic density function,  $\varrho(r)$ , was obtained by the Fourier transformation of  $I_{\text{Ge}}(K)$  according to the following equation;

$$4\pi r^2 (\varrho(r) - \varrho_0) = (2r/\pi) \int_0^\infty K (I(K) - 1) \sin Kr \, dr \quad (1)$$

where,  $\varrho_0$  = mean atomic density,  $I(K) = I_{\text{eu}}/f^2$ ,  $I_{\text{eu}}$  = observed intensity in electron units,  $f$  = atomic scattering factor. The essential features of  $4\pi r^2 \varrho(r)$  were obtained from a three dimensional ball and spoke model. This was constructed from a basic unit of seven atoms which contained features of the white tin crystal structure, i.e. a central atom with four close neighbours at the corners of a flattened tetrahedron and two additional atoms at a slightly longer near neighbour distance. The complete model was made by fitting these units together using the longer near neighbour distance between the atoms composing different units, slight distortions of the units were permitted in order to fill space without leaving voids. This model gave the correct first peak position of 2.8 Å and an area under the first main peak of  $4\pi r^2 \varrho(r)$  of 8.0 atoms.

## 2. Proposed Model

The present model is similar to the earlier one in that it suggests that germanium atoms in a liquid may come together to give either long or short near neighbour distances. The majority of atoms have the longer near neighbour distances, while a minority exhibit the short distances. If the atoms which have these different near neighbour distances are designated A and B, A atoms have longer near neighbour distances than B atoms it is possible to divide up the liquid into different atomic density functions<sup>8</sup>. Thus the total atomic density,  $\varrho_T(r)$ , may be expressed in terms of the separate, or partial, density functions,  $\varrho_{AA}(r)$ ,  $\varrho_{BB}(r)$ ,  $\varrho_{AB}(r)$  and  $\varrho_{BA}(r)$ .

$$\varrho_T(r) = c_A \varrho_{AA}(r) + c_B \varrho_{BB}(r) + c_A \varrho_{AB}(r) + c_B \varrho_{BA}(r), \quad (2)$$

where  $c_A$  is the atomic concentration of the A type atoms, it can also be shown that

$$c_A \varrho_{AB}(r) = c_B \varrho_{BA}(r).$$

A further proposal to be incorporated in the model is that for any B type atom its interaction with A type atoms is such that  $\varrho_{BA}(r)$  may be approximated by  $\varrho_{AA}(r)$ . To make this situation clear a two dimensional representation is shown in Figure 1. Here the near neighbour separations of the hard disc centres are ( $D$  = diameter of disc)  $D_A$  or  $D_B$  and  $(D_A + D_B)/2$  has been excluded. In conformity with the earlier model B type atoms are represented in Fig. 1 as members of groups of four atoms, these groups play no part in the present model because it is suggested that this liquid does not sustain rigid atomic groupings. Thus, in the present model it is

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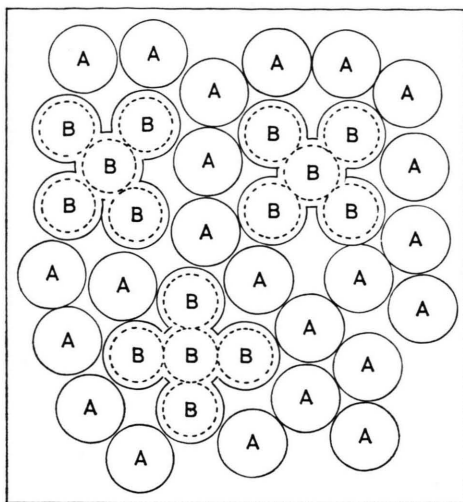


Fig. 1. Two Dimensional Diagram of Liquid Germanium. A type atoms, only long near neighbour distances. B type atoms, some short near neighbour distances.

postulated that component atomic density functions tend to two distinct limits,  $\rho_{AA}(r)$  and  $\rho_{BB}(r)$ . Further, each distribution may be represented by a hard sphere density function. Clearly the model could be tested by combining these distributions together, as in Eq. (2), and then comparing  $\rho_T(r)$  with the experimental  $\rho(r)$ . However, it is well known that the experimental  $\rho(r)$  are subject to errors which make their detailed interpretation and comparison unreliable<sup>9</sup>. It is better to work in  $K$  space and compute the interference function directly from any model<sup>11</sup>.

### 3. The Equation for Superposition of Interference Functions

To work in  $K$  space partial density functions must be linked with partial interference functions<sup>5, 8</sup>, this can be done using the following equations.

$$I_{AA}(K) = 1 + \int_0^\infty 4\pi r^2 \{ [\rho_{AA}(r)/c_A] - \rho_0 \} \cdot \{\sin Kr\}/Kr dr, \quad (4a)$$

$$I_{BB}(K) = 1 + \int_0^\infty 4\pi r^2 \{ [\rho_{BB}(r)/c_B] - \rho_0 \} \cdot \{\sin Kr\}/Kr dr, \quad (4b)$$

$$I_{AB}(K) = 1 + \int_0^\infty 4\pi r^2 \{ [\rho_{AB}(r)/c_B] - \rho_0 \} \cdot \{\sin Kr\}/Kr dr. \quad (4c)$$

The total interference function,  $I_T(K)$ , is defined as;

$$I_T(K) = 1 + \int_0^\infty 4\pi r^2 [\rho_T(r) - \rho_0] [\sin Kr]/Kr dr. \quad (5)$$

By making use of Eq. (2), with the simplification that  $c_A \rho_{AB}(r) = c_B \rho_{BA}(r)$ , and Eqs. (4a), (4b), and (4c) it is possible to show;

$$I_T(K) = c_A^2 I_{AA}(K) + c_B^2 I_{BB}(K) + 2c_A c_B I_{AB}(K). \quad (6)$$

In the model, that has just been presented,  $\rho_{BA}(r) = \rho_{AB}(r) = \rho_{AA}(r)$ , so it is justified to take  $I_{AB}(K) = I_{AA}(K)$ , thus, Eq. 6 may be simplified to give the total interference function as the superposition of two partial interference functions.

$$I_T(K) = c_A(1 + c_B)I_{AA}(K) + c_B^2 I_{BB}(K). \quad (7)$$

### 4. Results and Conclusions

Because of the good agreement found between  $I(K\sigma)$  for  $\eta = 0.45$  and  $I(K)$  for some liquid metals, mentioned in the Introduction, it was decided to use this value for the initial packing density for the hard sphere interference functions used to represent  $I_{AA}(K)$  and  $I_{BB}(K)$  in Equation (7). This packing density was varied, and both the hard sphere diameters and concentrations were adjusted, to give agreement with the characteristic form of the first peak of  $I_{Ge}(K)$  at 1047 °C. Best agreement was found with only a small change in the packing density to  $\eta = 0.41$  with  $\sigma_A = 2.70$  Å,  $\sigma_B = 2.07$  Å and  $c_A = 0.58$ .  $I_T(K)$  corresponding to these values is shown on Figure 2. It can be seen that in the region of the

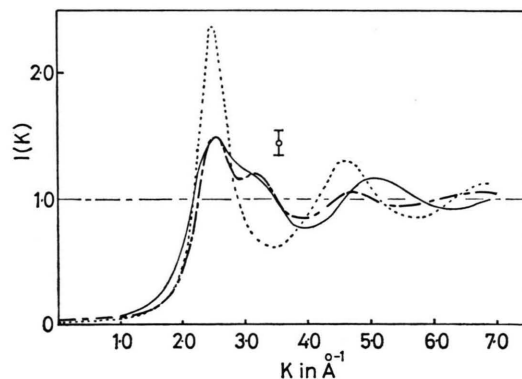


Fig. 2. Interference Functions. —  $I_{Ge}(K)$  at 1047 °C,  $\Phi$  experimental error,  $\pm 7\%$ ; ----  $I(K\sigma)$ ,  $\eta = 0.45$ ; -.-  $I_T(K)$ ,  $\sigma_A = 2.70$  Å,  $\sigma_B = 2.07$  Å,  $\eta = 0.41$ ,  $c_A = 0.58$ .

first main peak  $I_T(K)$  is within the experimental error of  $I_{Ge}(K)$  and, therefore, provides better agreement than the single hard sphere interference function,  $I(K\sigma)$ , for  $\eta = 0.45$ . The largest contribution to the first part of the main peak came from  $I(K\sigma_A)$  and  $I(K\sigma_B)$  gave the largest contribution to the shoulder.

In support of the present work it should be mentioned that an analogous situation to the one

discussed here has been verified<sup>10</sup> by neutron diffraction from isotopically substituted molten copper-tin alloys. The unlike partial interference function,  $I_{\text{CuSn}}(K)$ , was similar to  $I_{\text{CuCu}}(K)$  and the liquid alloy could be represented by only two partial interference functions.

In conclusion, it is clear from this calculation that the large angle x-ray interference function for liquid

germanium at 1047 °C may be explained in terms of a double hard sphere structure. It is not intended in the present note to speculate about the nature of the interatomic bonding which gives these different structures (i.e. metallic or covalent) until more work has been done to establish the applicability of the model.

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<sup>11</sup> A. similar real space model, using a double structure, has been proposed by H. Richter and G. Breitling, *Z. Naturforsch.* **16a**, 187 [1961].

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## Berichtigung

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P. Brill, Zum paramagnetischen Verhalten von Pd/Ag/Fe-Legierungen, *Z. Naturforsch.* **30a**, 645 [1975].

Der überwiegende Teil dieser Arbeit entstand im Rahmen einer Dissertationsarbeit am Physikalisch-Chemischen Institut unter Anleitung von Prof. Dr. J. Voitländer. Die Arbeit wurde durch eine Sachbeihilfe gefördert, die Herrn Prof. Dr. J. Voitländer von der Deutschen Forschungsgemeinschaft gewährt wurde. Hierfür möchte ich Herrn Prof. Dr. J. Voitländer und der DFG danken.

Die hier gegebene Interpretation der Meßergebnisse erfuhr nur teilweise die Zustimmung von Prof. Dr. J. Voitländer.