A Double Hard Sphere Model of Liquid Semi-Metals:
Applications to Bismuth and Tin

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The double hard sphere model previously used to calculate the interference functions for liquid Ge, Sb and Ga has now been applied to Sn and Bi. The main features of the observed interference functions just above the melting points have been reproduced, within experimental error, by the superposition of two different partial interference functions represented by hard sphere functions with packing densities of 0.475 and 0.470 for Sn and 0.430 and 0.400 for Bi and respective hard sphere diameters; 3.030 Å and 2.420 Å: 3.335 Å and 2.450 Å. The model has been developed to give a qualitative picture of the bonding in the liquid with the short distance associated with possible overlap of p orbitals. Further, this model has been shown to be in keeping with an alternative employing a ledge type interatomic potential by referring to the measured compressibilities.

1. Introduction

In the previous papers on Ge [1], Sb [2], and Ga [3] it has been shown that a double hard sphere model can be used to calculate, within experimental error, the observed interference function $I(K)$ $[K = (4\pi \sin\theta)/\lambda, 2\theta = \text{scattering angle}, \lambda = \text{wavelength of incident radiation}]$. There is a common feature which links together the interference function of Ge, Sb and Ga, on one hand, and on the other, Sn and Bi, the two liquid metals discussed in the present work.

This feature is a subsidiary maximum or shoulder on the K side of the first main peak. The double hard sphere model which has been used to reproduce interference functions which show this feature consists of the following proposals: (1) there are two possible near neighbour distances, r_{AA} and r_{BB}, with $r_{AA} > r_{BB}$, (2) the interaction between A and B species is the same as that between the A species, so $r_{AB} = r_{AA}$. Using these proposals the total interference function, $I_T(K)$, can be calculated and is composed of only two partial interference functions, $I_{AA}(K)$ and $I_{BB}(K)$, because since $r_{AB} = r_{AA}$,

$I_{AB}(K) = I_{AA}(K)$, thus it has been shown [1] that $I_T(K)$ may be written as

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

$c_A = $ atomic fraction of species which has the longest distance of atomic separation.

Since the first note in this series was published other work [4] has appeared which suggests that the interatomic potential in molten semi-metals has a ledge or step. This potential has been used to calculate the interference function for molten Bi. In the present work this result will be compared with that from the double hard sphere model. Both the ledge potential and double hard sphere model will be shown to be plausible in the light of known compressibility data on liquid semi-metals. Further, the double hard sphere model will be expanded by linking it, through the results of electron spectroscopy, to the bonding known to exist in the crystalline solid.

2. Model Interference Function Compared with Experiment

The experimental interference functions, $I_{\exp}(K)$, to which $I_T(K)$ was matched, was chosen because tabulated values were available. For Sn the neutron diffraction data of North [5], taken at $250\,°C$, were chosen, while for Bi the x-ray diffraction measurements at $300\,°C$, obtained by the present author [6], were used. As in earlier work, to obtain agreement between $I_T(K)$ and $I_{\exp}(K)$ the partial interference functions used in Eq. (1) were assumed to be given by hard sphere interference functions, $I(K, \sigma, \eta)$, $\sigma = $ hard sphere diameter, $\eta = $ packing density [7]. σ, η, and c for each atomic species were all varied in a systematic way until the best possible agreement with $I_{\exp}(K)$ was found. A perfect match over all values if K was not possible, but best agreement was sought in the region of the main and subsidiary maxima where the smallest error ($\pm 5\%$) in $I_{\exp}(K)$ existed. From Fig. 1 and Fig. 2 it can be seen that there is good agreement between $I_T(K)$ and $I_{\exp}(K)$ for both Sn and Bi if:

$$\eta_A^{Sn} = 0.475, \quad \eta_B^{Sn} = 0.470; \quad \sigma_A^{Sn} = 3.030 \text{ Å},$$
$$\sigma_B^{Sn} = 2.420; \quad c_A^{Sn} = 0.67 .$$
$$\eta_A^{Bi} = 0.430, \quad \eta_B^{Bi} = 0.400; \quad \sigma_A^{Bi} = 3.225 \text{ Å},$$
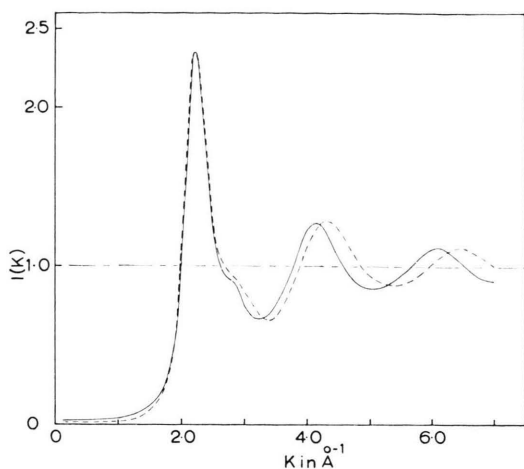$$\sigma_B^{Bi} = 2.450; \quad c_A^{Bi} = 0.60 .$$

Fig. 1. Interference functions for liquid Sn. --- $I_{Sn}(K)$ at 300 °C [5]. ——— $I_T(K)$, $\eta_A = 0.475$, $\eta_B = 0.470$; $\sigma_A = 3.030$ Å, $\sigma_B = 2.240$ Å; $c_A = 0.67$.
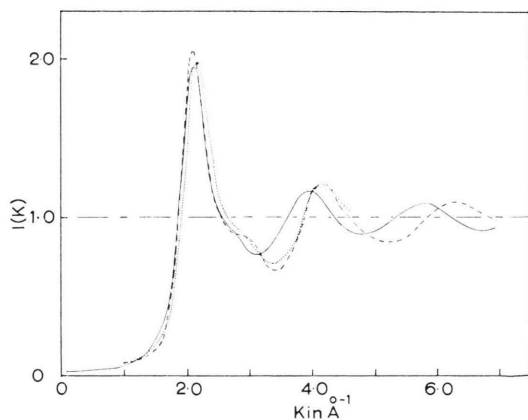

Fig. 2. Interference functions for liquid Bi. --- $I_{Bi}(K)$ at 232 °C [6]. ——— $I_T(K)$, $\eta_A = 0.430$, $\eta_B = 0.400$; $\sigma_A = 3.225$ Å, $\sigma_B = 2.450$ Å; $c_A = 0.60$. ···· $I(K)$ from ledge potential [4].

It must be pointed out that the Ashcroft and Lekner [7] hard sphere interference functions give best agreement with simple liquid metals, such as Cu, in the region of the first main peak. Bletry [8] has calculated a soft sphere interference function which gives good agreement over a wider range of K for Cu and will afford an opportunity to use a more realistic component interference function in place of $I(K, \sigma, \eta)$.

3. Discussion

In the solid crystalline form each atom of Sn and Bi has six near neighbours and their structures are typical of semi-metals because they are not as close packed as metals such as Cu, Na or K. White Sn has an A 5 tetragonal structure with four atoms at a close distance of 3.016 Å and two further atoms at 3.175 Å. Crystalline Bi is of the A 7 hexagonal type and can be looked upon as a layered structure with each atom having three short near neighbour distances of 3.105 Å within the layers and three more at 3.474 Å in the adjacent layer. The dual nature of these structures is a reflection of bonding of the atoms. Krebs [9] has suggested that the directional character of the crystal structure of white Sn can be explained by the hybridization of the p and d orbitals, which give the four short distances, while the longer distances are due to the overlap of p orbitals. The hybrid bonding functions for Bi are made up of primarily p type wave functions and result in almost orthogonal bonds giving the shorter bond within the layers. The longer bond, at almost 180° to the shorter bond is where the bonding function is smaller. On melting the density of Sn increases by 2.6% while for Bi there is a decrease of 3.4% [10]. A very important point is that both liquids tend to become more free electron like than the crystalline solid [10]. It is the contention of the present work that the directional p-type character of the bond is weakened in the liquid but not completely lost. It is therefore necessary to show that some property of p valence states remains unchanged when the solids and liquids are compared. Measurements which are sensitive to both s and p valence states are the electron energy distribution curves obtained by x-ray or UV photoemission. It has been shown that these curves, when suitably corrected, can be related to the density of valence states. Experiments have clearly demonstrated that s and p regions of the valence band for crystalline Sn [11] and Bi [12] are separate and that this separation persists in the liquid phase [13, 12]. Thus any bonding in the liquid could be expected to have the p type directional character of the solid, but it must be explained how it can operate in the liquid. An earlier description of another liquid semimetal, Sb, can be used as a starting point [14]. It was suggested that a mobile bonding system operates, with the bond alternating between p-type and (sp)-hybrid, with thermal energies involved in the transition between one bond form and another. The objective of this model was to show that the short range order was predominantly of the NaCl

type, hence the importance of the orthogonal p orbitals. In the present work the broad picture of a mobile bonding system is accepted, but the view of the short range order is too specific. The present author's view can be described as follows. In the crystalline solid each atom can be regarded as being at the centre of its own regular Voranoi polyhedron (a figure formed by planes which bisect the lines connecting atomic centres). In the liquid each atom has its own Voranoi polyhedron, but it is no longer regular though of the same volume since the change in density is small on melting. In this polyhedron the atom is unchanged with essentially similar bonding characteristics. The short interatomic distance comes about only when the bond directions of a pair of adjacent atoms are correctly orientated. It is by this mechanism that the important feature of the model, given in the Introduction, i.e. $r_{AB} = r_{AA}$. This means that if a pair of atoms bond together with the short distance of atomic separation, the remaining surrounding atoms do not take up the short distance but stay at the longer distance because it is unlikely that the orientation of their bonding p electrons will be correct. The main A type separations of the atoms would correspond to non-directional s-type metallic bond.

The model that has been used here began [1] as an extension of the measurements on Cu_6Sn_5 by Enderby, Egelstaff and North [15] where the partial interference function, $I_{CuSn}(K)$, was found to be similar to $I_{CuCu}(K)$. Recently, Bletry [16] has published a geometrical model for alloys in which disordered alloys are discussed by way of chemical packing algorithms. The existing algorithms appear too simple to cover Cu_6Sn_5 and the present work since we have attempted to show that mutual orientation of near neighbours is important in determining interatomic distances for Sn. Thus, this effect would have to be taken into account if a geometric model of Cu_6Sn_5 were built.

It is now necessary to see if the potential proposed by Silbert and Young [4] is compatible with the double hard sphere model. From the discussion of the bonding it is clear that the potential will be a function of the mutual orientation of the atoms. If a spacial average over near neighbours in the crystal were taken, this would lead to a potential with a double minimum, as sketched in Figure 3. Moreover, it is suggested that this potential operates in the liquid. The precise analytic form of this potential is
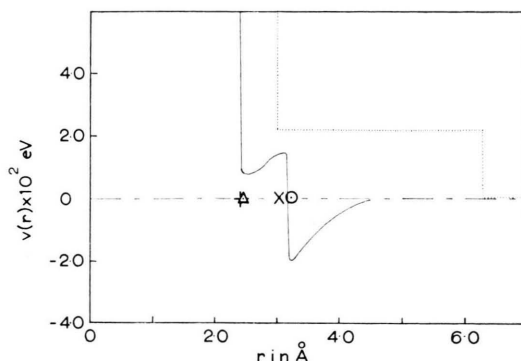

Fig. 3. Interatomic potentials, $v(r)$. $\cdots$ Ledge potential [4]. —— Sketch of proposed potential for Bi. $\times$ σ_A^{Sn} + σ_B^{Sn}; $\odot$ σ_A^{Bi}, $\triangle$ σ_B^{Bi}.

not clear, but as can be seen from Fig. 3 this is similar to that proposed by Silbert and Young [4]. The resulting interference function is included on Fig. 2 and as can be seen the main subsidiary maxima are correctly reproduced. These results have been confirmed by Monte Carlo calculations [17], however a subsidiary maximum also appears on the second peak which is neither a feature of the experimental data used in the present work nor predicted by the present model. If a potential with either a double minimum or a step or ledge form operated in the liquid it would be expected that the compressibility would be larger than for a liquid in which the potential had a single minimum, as in a close packed metallic liquid. The compressibility, B, is related to the speed of sound, s, by

$$B = N/M\,s\,.$$

where N = number of atoms, M = ionic mass. For a liquid metal interacting with a screened Coulomb potential it has been shown that [18] the longitudinal acoustic velocity, $c' = [(2ZE_F)/3\,M]^{1/2}$, where Z = valency, E_F = free electron value of the Fermi Energy. For Sn $c' = 4630$ m s^{-1} and $s = 2464$ m s^{-1}; for Bi, $c' = 3940$ m s^{-1} and $s = 1649$ m s^{-1} [19]. Since the speed of sound in both cases is smaller than predicted this implies that B is larger than would be expected assuming Coulombic interaction and in agreement with the proposal given above.

From the arguments set out in this section, it is concluded that the interaction between Sn atoms and Bi atoms in their respective liquids is more complex than, say, between liquid alkali metals and

indicates that the double hard sphere model may be correct. In addition, it seems likely that part of the bonding between these semi-metals has a co-valent component and this may be associated with a short distance of atomic separation.

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