A Model of the Structure of Liquid Antimony

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The interference function from liquid antimony at 600 °C, obtained by Waseda and Suzuki, has been reproduced using a model based on two hard sphere interference functions (packing density, 0.41 diameters 3.11 Å and 2.33 Å). Agreement obtained using the model is better than that existing between various independent diffraction measurements.

1. Introduction

In an earlier note[1] a model of liquid germanium was proposed from which an interference function, defined in[1], was computed and good agreement was obtained with the experimental interference function $I_{\mathrm{Ge}}(K)$ $[K=(4\pi\sin\theta)/\lambda,\ 2\theta=\text{scattering angle},\ \lambda=\text{wave length of incident radiation}]$. This model consisted of assuming that the interactions between the atoms in the liquid are of two types which give rise to long, A type, and short, B type, distances of atomic separation. The characteristic restriction included in this model was that the A – B interactions are the same as the A – A type interactions.

In the solid state the A 7 tetragonal structure of antimony can be looked upon as a type of double structure, because each atom has two sets of three near neighbours at 3.36 Å and 2.90 Å. It is not suggested that this structure is carried over unchanged into the liquid state, but the atoms could interact in a similar way to provide long and short distances of atomic separation. Additional evidence in favour of applying this model to liquid antimony is provided by an examination of the published x-ray and neutron scattering data[2, 4–8]. Even the earliest measurement[2] of the diffraction pattern showed a subsidiary maximum as a shoulder on the high K side of the first main peak and distinguished it from those of simpler liquid metals (e.g. Na, K, Au). A similar shoulder was present on the interference function of germanium and was correctly reproduced by the proposed model[1].

The idea of a double structure in liquid antimony is not new, it was first proposed by Richter and Breitling[3], using the experimental results of Müller and Hendus[2]. However, evidence for this double structure in the liquid state was obtained from the peak positions of the interference function found at large values of K. Unfortunately, these peaks occurred in the region of the interference function which had the lowest accuracy. In addition, the peaks used were broad and not very well defined, so the model did not have a very firm base.

Measurements which followed[4–8] those of Müller and Hendus[2] gave essentially the same shape of pattern, with a main and subsidiary peak, but the values of K at which they appeared were variable, as can be seen from the table. Also, wide variations in the intensity can be found, and they are particularly noticeable between the recent neutron measurements of Waseda and Suzuki[7] and Knoll and Steeb[8], as indicated on the figure. It is not possible, however, to make an assessment of the relative reliabilities of the many measurements, so it was decided to apply the model to obtain the best possible agreement with the only published tabulated interference function[7]. Waseda and Suzuki[7] published tabulated values of the neutron structure factor, $a(K)$, which is equivalent to the interference function, $I_{\mathrm{Sb}}(K)$, defined earlier[1].

2. Model Interference Function Compared with Experiment

In[1] it was shown that the model interference function, $I_{\mathrm{T}}(K)$, could be written in terms of the partial interference functions, $I_{\mathrm{AA}}(K)$ and $I_{\mathrm{BB}}(K)$ due to the A and B species, by the following equation,

$$I_{\mathrm{T}}(K)=c_{\mathrm{A}}(1+c_{\mathrm{B}})I_{\mathrm{AA}}(K)+c_{\mathrm{B}}^{2}I_{\mathrm{BB}}(K),$$

where c_{A} and c_{B} were the atomic fractions of A and B species. It was found[1] that an adequate model $I_{\mathrm{T}}(K)$ could be obtained if $I_{\mathrm{AA}}(\mathrm{K})$ and $I_{\mathrm{BB}}(K)$ were assumed to be given by the Ashcroft and Lekner[9] hard sphere interference function, $I(K\sigma,\eta)$, where σ was the hard sphere diameter and η the

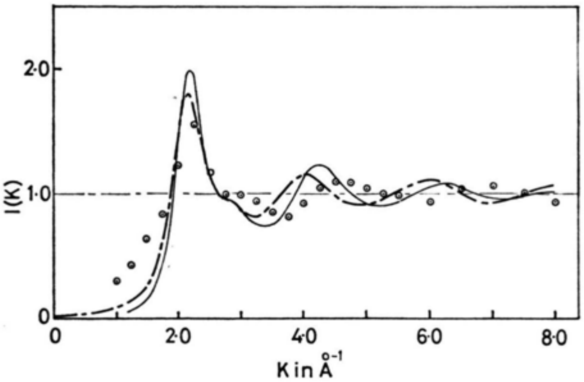

Fig. 1. Interference functions. —— $I_{\mathrm{Sb}}(K)$ at 660 °C by Waseda and Suzuki[7]. – – – $I_{\mathrm{T}}(K)$, $\sigma_{\mathrm{A}}=3.11$ Å, $\sigma_{\mathrm{B}}=2.33$ Å, $\eta=0.41$, $c_{\mathrm{A}}=0.60$. ⊙ points read from the published graph of $I_{\mathrm{Sb}}(K)$ by Knoll and Steeb[8].

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packing density. The same assumption was made in the present work. To obtain agreement with $I_{\mathrm{Sb}}(K)$ at 660 °C[7], σ_{A}, σ_{B}, η and c_{A} were all varied in a systematic way. Good agreement (see Fig. 1) was obtained when $\sigma_{\mathrm{A}} = 3.11$ Å, $\sigma_{\mathrm{B}} = 2.33$ Å, $\eta_{\mathrm{A}} = \eta_{\mathrm{B}} = 0.41$ and $c_{\mathrm{A}} = 0.60$. If the diameters used in the model are compared with the crystalline interatomic distances, reductions on melting are found ($\sigma_{\mathrm{A}} < 3.36$ Å, $\sigma_{\mathrm{B}} < 2.90$ Å). This behaviour is consistent, in a qualitative way, with the contraction found on melting[10], and is a factor in favour of the model.

Table 1.

Author	Ref. No.	Temp. °C	1st peak position Å^{-1}	Subsidiary peak position Å^{-1}
Müller and Hendus	2	665	2.17	3.25
Dutchak	4	640	2.04	3.15
Lashko and Poltavtsev	5	685	1.93	2.68
Gruber and Krebs	6	620	2.09	3.02
Waseda and Suzuki	7	660	2.15	3.00
Knoll and Steeb	8	641	2.20	3.30

3. Discussion

The present work has shown that the double hard sphere model can be extended from germanium to antimony. It is, therefore, worth looking for a common parameter linking the two models. This can be found in the packing density, η, which was set at 0.41, for both models. It has been shown[9] that η ($= 0.45$) is also the common factor linking $I(K\sigma, \eta)$ which agree with the experimental $I(K)$ of the simple liquid metals (e.g. Na, K, Au).

As a result of this extension of the model it is appropriate to speculate about the nature of the bonding between A and B species in both liquid germanium and antimony. The larger, A type, separations are due to positive metal ions screened by free valence electrons. The smaller, B type, separations are due to localization of valence electrons into a form of covalent bond. Localization of electrons cannot be stable with time as B type interactions move through the liquid. It should be noted that A type species are in the majority in both liquids ($c_{\mathrm{A}}^{\mathrm{Ge}} = 0.58$, $c_{\mathrm{A}}^{\mathrm{Sb}} = 0.60$). This must be the reason why both liquids have an essentially free electron Hall coefficient[11]. More detailed calculations and interpretation must await better experimental interference functions, particularly for liquid antimony.

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