Original Papers

phys. stat. sol. (b) **159**, 545 (1990)

Subject classification: 61.25; S4

Departement of Physical Chemistry, Jadavpur University, Calcutta[1])

Computation of the Structure Factors of the Peculiar Metals Sb, Bi, Ga, and Sn Using Lebowitz's Solution of Hard-Sphere Mixtures

By

R. V. GOPALA RAO and A. SATPATHY

The peculiar metals Bi, Sb, Ga, and Sn, which show a subsidary right-hand shoulder in the structure factor at or near the melting point, are studied through Lebowitz's solution of hard-sphere mixtures by assuming the liquids to be a mixture of two types of species of different diameters. The agreement between theoretical and experimental structure factors throughout the whole range of momentum space is excellent. It is found that metalloids like Bi and Sb can be treated as simple hard-sphere mixtures of two different species while in the case of metals like Ga and Sn a square well attractive tail is used as a perturbation of the hard-sphere mixture.

Die besonderen Metalle Bi, Sb, Ga und Sn, die eine rechte Nebenschulter im Strukturfaktor bei oder in der Nähe des Schmelzpunktes besitzen, werden mit der Lebowitzschen Lösung der Mischung harter Kugeln untersucht, wobei angenommen wird, daß die Flüssigkeiten eine Mischung zweier Species mit unterschiedlichen Durchmessern ist. Die Übereinstimmumg zwischen theoretischen und experimentellen Strukturfaktoren im gesamten Impulsraum ist ausgezeichnet. Es wird gefunden, daß Metalloide, wie Bi und Sb, wie einfache Mischungen harter Kugeln zweier verschiedener Spezies behandelt werden können, während im Falle von Metallen, wie Ga und Sn, ein anziehender Rechteckpotentialausläufer als Störung der Mischung der harten Kugeln benutzt wird.

1. Introduction

The structure factor of liquid metals can be broadly classified into the following categories:

a) The first type can be considered as simple liquid metals if they show a symmetrical principal peak in the structure factor.

Alkali, alkaline earth, noble, and transition metals exhibiting a symmetrical main peak, belong to this group.

b) Metals like Zn, Cd, and Hg show an asymmetric main peak at or near the melting point and hence can be termed as non-simple liquid metals.

c) In the third group a subsidiary shoulder in the main peak is observed. Ga, Sn, Ge, etc. do exhibit this phenomenon and are called peculiar liquid metals.

Several authors [1 to 4] have tried to explain the subsidiary shoulder exhibited by metals like Bi, Sb, Ga, Sn, etc. by various models. Orton assumed two types of atoms with different diameters and, with certain assumptions [5, 6], computed structure factors. The structure factors were evaluated through the method of Ashcroft and Leckner [7] which uses the Wertheim-Thiele [8] solution applicable to a system of single species. The results show only qualitative agreement with experiment. The method due to Canessa et al. [3, 4] contains several unphysical parameters and the results in all the above cases are also not satisfactory.

---

[1]) Calcutta 700032, India.

Recently Zou et al. [9] calculated the structure factors of the peculiar metals Bi, Sb, Ga, Sn. Their results are satisfactory and in very good agreement with experiment. However, they make the unphysical assumption of σ_i and η_i to be independent parameters and use the Wertheim-Thiele solution of a one-component system in which σ and η are not independent, while the system used by Zou et al. [9] consists of two species with two different diameters. Thus a theoretically acceptable method is to use a binary system of hard spheres a perturbation method wherever necessary through the use of the mean sphere model approximation (MSMA). However, we may add that the work of Xian-Wu Zou et al. is a good beginning. In this paper we demonstrate the application of the well-known Lebowitz [10] solution of hard-sphere mixtures in the generation of the structure factor of four peculiar metals. At the outset we are happy to say the results are in excellent agreement with experiment.

2. Method

As these peculiar metals occur in several polymorphic forms [9, 11] we assume that these metals retain some of the characteristics of polymorphism at or near the melting point. Like all others [1 to 4] we assume the existence of two types of species and unlike others [1, 2] we take into consideration the interaction between all the species. Thus we will have (11) type, (22) type, and (12) type interactions between species 1 and 2. We use the well-known binary mixture solution of Lebowitz for hard spheres [10].

At this juncture it is important to point out that some peculiar metals which are really metalloids like Sb and Bi can be considered as consisting of a mixture of hard spheres in each metal, while in the case of metals like Ga and Sn some attraction is found to exist and hence the Lebowitz solution of hard-sphere mixtures has to be perturbed by an attractive tail.

Thus to generate the structure factors in the case of metalloids like Sb and Bi a simple hard-sphere mixture should work, while in the case of metals like Ga and Sn square-well attraction has to be taken into account.

Thus the $C_{ij}(r)$ according to Lebowitz is given by

$$-C_{ij}(r) = a_i + b_i r + dr^3 ; \qquad r < \sigma_i , \tag{1}$$

$$a_1 ; \qquad r < \lambda , \tag{2}$$

$$-C_{12}(r) = a_1 + \frac{1}{r}[b(r-\lambda)^2 + 4\lambda d(r-\lambda)^3 + d(r-\lambda)^4] ; \quad \lambda < r < \sigma_{12} , \tag{3}$$

$$0 ; \qquad r > \sigma_{12} \tag{4}$$

for simple hard-sphere mixtures, while for hard-sphere mixture with an attractive tail (4) has to be modified as follows:

$$C_{ij} = -\beta\Phi_{ij} = \beta\varepsilon_{ij} , \qquad \sigma_{ij} \leqq r \leqq A_{ij}\sigma_{ij} , \tag{5}$$

$$0 ; \qquad r > A_{ij}\sigma_{ij} . \tag{6}$$

Here the various symbols have been extensively described in detail in our previous papers [12 to 15].

In order to estimate the fraction of the first species C_1, we use the Kirkwood-Bouff equation of compressibility, namely,

$$S(0) = \varrho k_B T \chi_T = [1 - C_1\varrho_{11}\hat{C}_{11}(0) - (1 - C_1)\varrho_{22}\hat{C}_{22}(0) - 2\varrho_{12}C_1(1 - C_1)\hat{C}_{12}(0)]^{-1} , \tag{7}$$

Table 1
Molecular parameters and input data used to calculate $S(k)$ for Bi and Sb

metal	T (K)	σ_{11} (10^{-1} nm)	σ_{12} (10^{-1} nm)	σ_{22} (10^{-1} nm)	atomic fraction C_1
Bi	573.0	2.98	3.00	3.18	0.18
Sb	933.0	2.40	2.65	3.05	0.13

where the symbols have been already explained [12 to 15]. In this particular case χ_T is the compressibility of a single metal which is involved in (7). We scan a certain set of values of σ_{11}, σ_{22}, and C_1, to obtain the correct $S(0)$.

We select the best set to produce the total structure factor which generates the experimental structure factor of the peculiar metal. The total structure factor is obtained through the following equation [14]

$$S(k) = \sum_{i=1}^{2} \sum_{j=1}^{2} (C_i C_j)^{1/2} \frac{f_i(k) f_j(k)}{C_1 f_1^2(k) + C_2 f_2^2(k)} S_{ij}(k), \tag{8}$$

where $S_{ij}(k)$ are the partial structure factors. The evaluation of which has already been described [11 to 14].

The best possible parameters obtained for Sb and Bi are given in Table 1.

In the liquids where attraction is also present we select in addition ε and A, the potential depth and the attractive breadth, respectively, along with σ_{11}, σ_{22}, and C_1.

3. Results and Discussion

The structure factors of Bi and Sb are given in Fig. 1 while those of Ga and Sn are shown in Fig. 2. It is gratifying to note that the present treatment gives excellent results in agreement with experiment [16, 17]. It may be mentioned at this point that in a metal, even though

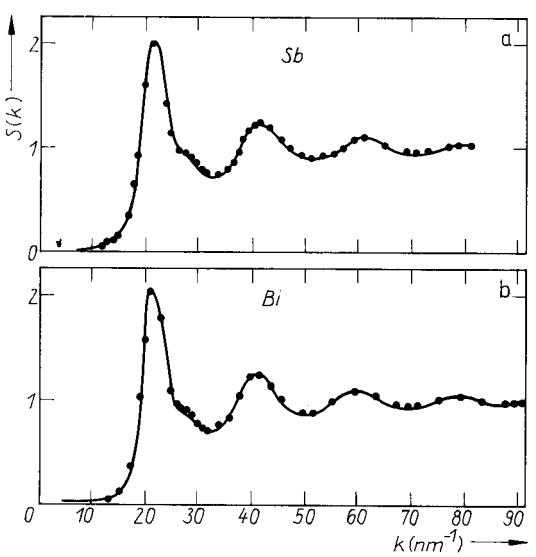

Fig. 1. Structure factors of liquid a) Sb at 660 °C and b) Bi at 300 °C. ● experimental points, ——— present results

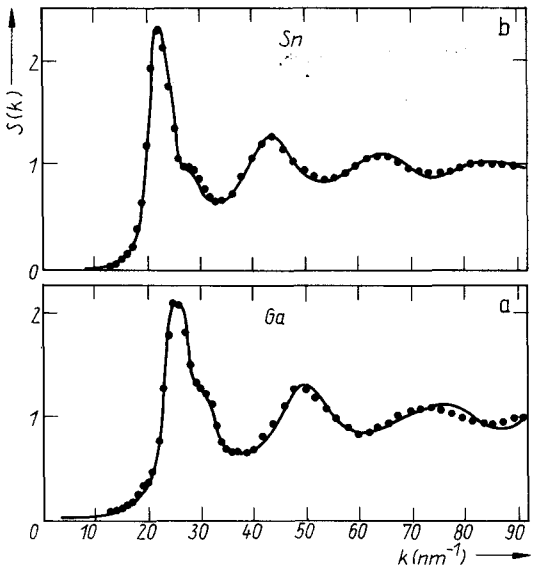

Fig. 2. Structure factors of liquid a) Ga at 50 °C and b) Sn at 250 °C, ● experimental points, ——— present results

two kinds of species exist, the potential depth ε and breadth A are found to be the same, in spite of the difference in the diameters of the species. The fractions of species 1 found are given in Tables 1 and 2.

It may be noticed from Tables 1 and 2 that σ_{12} is nearly $(\sigma_1 + \sigma_2)/2$ which is expected as they belong to the same metal. It is important to point out that even though (7) was used to obtain the potential parameters, they had to be slightly varied so as to generate the exact structure factor. Hence it is not expected that these potential parameters give the exact experimental $S(0)$ values [16, 17] as the primary purpose of the work is to generate $S(k)$ in the entire momentum space. Further $S(0)$ is connected through $C_{ij}(0)$ as can be seen from the Kirkwood-Buff equation and $C_{ij}(0)$ are very sensitive to σ_{ij} in the low-k region and hence $S(0)$ is not expected to be accurate if calculated from the present parameters. The results of $S(0)$ due to Xian-Wu Zou et al. who could generate good structure factors compare favourably with our calculated $S(0)$ values (Table 3).

Table 2
Potential parameters and input data used to calculate $S(k)$ for Ga and Sn

metal	T (K)	σ_{11} (10^{-1} nm)	σ_{12} (10^{-1} nm)	σ_{22} (10^{-1} nm)	A	ε/k_B (K)	atomic fraction C_1
Ga	323.0	2.50	2.56	2.70	1.73	140.0	0.90
Sn	523.0	2.86	2.95	3.05	1.75	150.0	0.68

Table 3
Theoretical and experimental values of $S(0)$ peculiar liquid metals Bi, Sb, Ga, and Sn

metal	T	theoretical		experiment
	(K)	present	[9]	
Bi	573.0	0.024	0.029	0.010
Sb	933.0	0.029	0.032	0.019
Ga	323.0	0.036	0.026	0.005
Sn	523.0	0.032	0.027	0.007

Acknowledgement

Sri A. S. would like to thank the Department of Science & Technology, Govt. of India for a SRF and RVGR is thankful to UGC for financial assistance.

References

[1] B. R. ORTON, Z. Naturf. **30a,** 1500 (1975).
[2] B. R. ORTON, Z. Naturf. **32a,** 332 (1977).
[3] E. CANESSA, D. F. MARIANI, and J. VIGNOLO, phys. stat. sol. (b) **124,** 465 (1984).
[4] E. CANESSA, D. F. MARIANI, and J. VIGNOLO, phys. stat. sol. (b) **126,** K1 (1984).
[5] B. R. ORTON, Z. Naturf. **31a,** 397 (1976).
[6] B. R. ORTON, J. Physique **41,** C8 280 (1980).
[7] N. W. ASHCROFT and J. LECKNER, Phys. Rev. **145,** 83 (1966).
[8] M. S. WERTHEIM, Phys. Rev. Letters **10,** 321 (1963).
[9] X. W. ZOU, Z. Z. JIN, and D. C. TIAN, phys. stat. sol. (b) **139,** 365 (1987).
[10] J. L. LEBOWITZ, Phys. Rev. **133,** A895 (1964).
[11] L. BOSIO, R. CORTES, and C. SEGAND, J. chem. Phys. **71,** 3595 (1979).
[12] R. V. GOPALA RAO and B. DAS GUPTA, Phys. Rev. B **32,** 6429 (1985).
[13] R. V. GOPALA RAO and B. M. SATPATHY, phys. stat. sol. (b) **110,** 273 (1982).
[14] R. V. GOPALA RAO and RATNA DAS, Phys. Rev. B **36,** 6325 (1987).
[15] R. V. GOPALA RAO and RATNA DAS, Phys. Rev. B **37,** 6908 (1988).
[16] Y. WASEDA and K. SUZUKI, phys. stat. sol. (b) **49,** 339 (1972).
[17] Y. WASEDA and K. SUZUKI, phys. stat. sol. (b) **47,** 581 (1971).

(Received September 4, 1989)