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and a Liquid Phase of a Metal**

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Phenomenological Relations between Solid Phases and a Liquid Phase of a Metal

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Part I

This report consists of two sections; one concerns the melting curves maxima, the entropy changes maxima during melting and the other concerns the electric resistances of bismuth as functions of pressure and temperature, which were observed in our experiments. The melting curves maxima can be explained phenomenologically by the two species model of Rapoport. Even though this model cannot be applied directly to bismuth, because the phase diagram is too complicated, the observed results of the electrical resistances seem to support the Rapoport's view concerning to the relations between solid phases and a liquid phase.

Introduction

There are a few theories which predict the melting curves. One of them is the Simon's equation¹⁾. With the assumption that the Grüneisen ratio is indeed constant, Slater²⁾ reformulated theoretically the equation from the Lindeman³⁾ law of melting. Recently Kraut and Kennedy⁴⁾ proposed the empirical equation to give the melting curves of the alkali metals except cesium. Following Ross⁵⁾, these equations can be derived by the statistical-mechanical manner and we can see that the difference of the forms of the two equations are due to the types of the potentials.

These equations do not predict the correct melting curves and give considerably high melting temperatures for most substances at high pressure. Moreover, since they are monotonous in the word of mathematics, they cannot explain the melting curves maxima.

Quite recently, Rapoport^{6) 7) 8)} proposed the unique model for molten metals. It is called the two species model and defined as follows⁸⁾. Suppose the liquid consists of two species, in the broad sense of the word, the one corresponding to the low pressure solid phase and the other to the high pressure phase respectively, and a species therefore is characterized by coordination number, nearest neighbor distance and bond type, the liquid is looked upon as a quasilattice with an average coordination number and can be treated by statistical mechanical methods by use of Bragg-Williams and Quasichemical approximations.

In this report we shall not give any criticisms to the two species model but derive some important facts. The phenomenological explanation of the melting curves maxima is included in them.

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The observed results of the electrical resistances of bismuth as functions of pressure and temperature seem to support the Rapoport's view. Here, the words "Rapoport's view" mean that a liquid consists of "Species".

Melting Curves Maxima on The Two Species Model

We shall restrict the detailed treatments to cesium and tellurium, because we can apply the numerical results of Rapoport^{7) 8)} directly to them. Following the two species model, the chemical potentials of two species (say A and B) are given by

$$\mu_A = \mu_A^\circ + RT \ln(1-x) + x^2 \omega \quad (1)$$

and

$$\mu_B = \mu_B^\circ + RT \ln x + (1-x)^2 \omega \quad (2)$$

respectively. The equilibrium condition is

$$\mu_A = \mu_B.$$

Hence we have

$$\Delta\mu^\circ = RT \ln \frac{x}{1-x} + (1-2x)\omega, \quad (3)$$

where

$$\Delta\mu^\circ = \mu_A^\circ - \mu_B^\circ.$$

Rapoport determined the relation between x , the mole fraction of the species B and pressure P from eq.(3), under the assumption for ω to satisfy the selfconsistency between $\Delta\mu^\circ$ and the electrical properties of the liquid under consideration.

The Gibbs' free energy of the liquid at pressure P and temperature T is

$$\begin{aligned} G &= \mu_A(1-x) + \mu_B x \\ &= \mu_A^\circ(1-x) + \mu_B^\circ x + RT \{(1-x) \ln(1-x) + x \ln x\} + x(1-x)\omega. \end{aligned} \quad (4)$$

If the pressure dependence of ω is negligible compared with others, the volume of the liquid is given by

$$V_l = \left(\frac{\partial G}{\partial P} \right)_T = (V_A)_l - x(V_B)_l, \quad (5)$$

where

$$\frac{\partial \mu_A^\circ}{\partial P} = (V_A)_s, \quad \frac{\partial \mu_B^\circ}{\partial P} = (V_B)_s$$

and

$$(\Delta V)_l = (V_A)_l - (V_B)_l > 0.$$

Hereafter l, s denote liquid and solid respectively.

Now, we shall introduce the assumption for the volume relation between the partial molar volume of a species and the volume of the corresponding solid phase, i, e ,

$$(V_A)_l = \frac{(V_A^\circ)_l}{(V_A^\circ)_s} \cdot (V_A)_s, \quad (6)$$

where $^\circ$ denotes the value at zero pressure. Moreover we assume that the ratio $(V_A^\circ)_l / (V_A^\circ)_s$ is indeed constant and independent of species and solid phases. $(\Delta V)_l$ then becomes

$$(\Delta V)_l = (V_A)_l - (V_B)_l = \frac{(V_A^\circ)_l}{(V_A^\circ)_s} \{(V_A)_s - (V_B)_s\}, \quad (7)$$

and eq.(5) becomes

$$V_l = \frac{(V_A^\circ)_l}{(V_A^\circ)_s} (V_A)_s - (\Delta V)_l x,$$

then being changed to the next form

$$\frac{V_l - V_s}{V_s^\circ} = \left\{ \Delta V_{s-l}^\circ \cdot \frac{V_s}{V_s^\circ} - (\Delta V)_l x \right\} / V_s^\circ, \quad (8)$$

where ΔV_{s-l} denotes the volume change during melting at zero pressure. We use the notation *s* instead of *A* in eq.(8). In fact there is no difference between the notation *A* and *s*. This will be understood later, when the calculations will be performed. According to the Rapoport's assumption that $(\Delta V)_l$ is roughly independent of pressure and temperature and using the observed values of $(V_A)_s$ and $(V_B)_s$ at room temperature^{9) 10)}, we can calculate $(\Delta V)_l$. Since the thermal expansion of a solid is generally very small compared with the volume change during melting, we may use the values of (V_s°) and V_s at room temperature instead of those at melting temperature in eq.(8). For cesium the values of ΔV_{s-l}° and $(\Delta V)_l$ are 1.81 cm³/mole and 3.42 cm³/mole^{9) 11)}. For tellurium they are 1.00 cm³/mole and 1.17 cm³/mole respectively^{10) 11)}. Then we can perform the calculations of the right hand side of e.q.(8) along the melting curves for cesium and tellurium. We give the numerical results by the dashed curves in Fig. 1 and Fig. 2. From these results and the Clausius-Clapayron equation, we

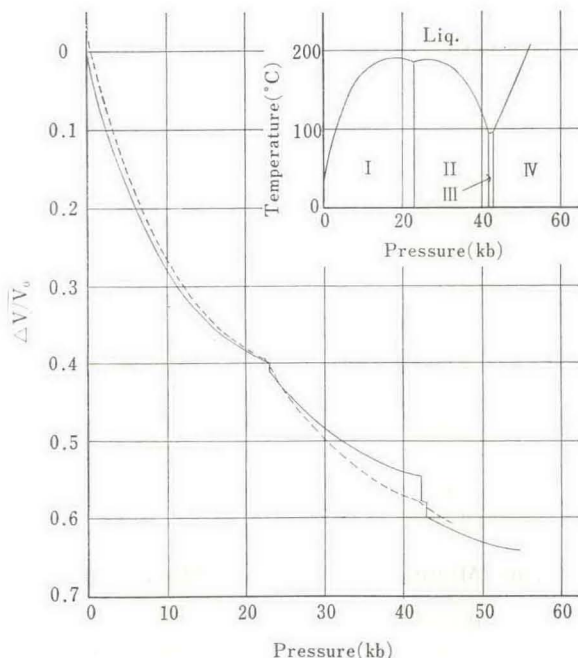


Fig. 1. The dashed curve shows the volume decrease of the liquid cesium at the melting temperature and the solid curve shows the volume decrease of the solid cesium at room temperature in terms of that at room temperature and pressure, V_0 as unity.

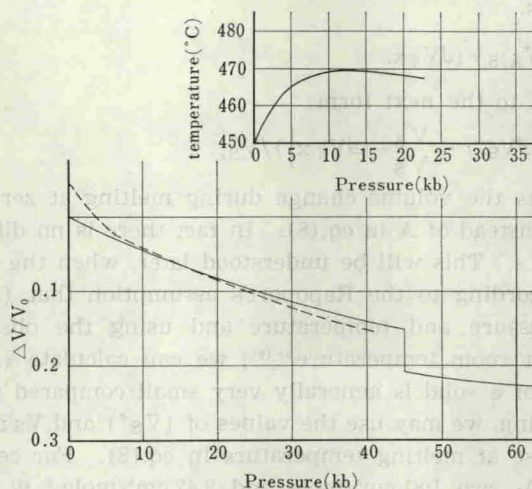


Fig. 2. The dashed curve shows the volume decrease of the liqued tellurium at the melting temperature and the solid curve shows the volume decrease of the solid tellurium at room temperature in terms of that at room temperature and pressure, V_0 as unity.

find that the agreements with the observed phase diagrams^{12) 13)} are quite good.

Now we shall derive the rough condition for a melting curve maximum from eq.(8). At this point the volume change during melting must be zero, hence, we have

$$x = \frac{\Delta V_{S-l}^{\circ}}{(\Delta V)_l} \cdot \frac{V_S^{\circ}}{V_S}$$

at this point.

If the melting curve maximum occurs below pressure P , x must be smaller than unit, i. e.,

$$\frac{\Delta V_{S-l}^{\circ}}{(\Delta V)_l} \cdot \frac{V_S^{\circ}}{V_S} \leq 1. \quad (9)$$

The values of ΔV_{S-l} 's have been obtained for most substances, hence, to calculate the left hand side we need only the value of V_S . Under the rough assumption, we may use a value of V_S at room temperature and the values of V_S 's have been obtained for many substances up to 80-100 kb. There are not many substances with the melting curves maxima in such pressure range, but the condition (9) is satisfied with those substances.

Entropy Changes during Melting on The Two Species Model

We shall derive the pressures at the entropy changes maxima along the melting curves for cesium and tellurium. We have the entropy of the liquid from eq.(4), i. e.,

$$S = - \left(\frac{\partial G}{\partial T} \right)_P = (S_A) - x_l (\Delta S)_l - R \{ (1-x) \ln (1-x) + x \ln x \},$$

where

$$(S_A)_l = -\frac{\partial \mu_A^{\circ}}{\partial T}, \quad (S_B)_l = -\frac{\partial \mu_B^{\circ}}{\partial T}$$

and

$$(\Delta S)_l = (S_A)_l - (S_B)_l.$$

Since the entropy change during melting is

$$\Delta S_m = S_l - S_s = (S_A)_l - x(\Delta S)_l - S_s - R\{(1-x)\ln(1-x) + x\ln x\},$$

the difference of ΔS_m along the melting curve is

$$d(\Delta S_m) = d(S_A)_l - dS_s - x d(\Delta S)_l - (\Delta S)_l dx - R\{-\ln(1-x) + \ln x\} dx. \quad (10)$$

Here it should be noted that $(S_A)_l$, $(\Delta S)_l$ and S_s are the values which depend on a species or a solid phase, that is, their variations depend predominantly on the variations of the thermal entropies. In general they are small and may be negligible compared with the variation of x . Therefore eq.(10) becomes

$$d(\Delta S_m) = -\left\{(\Delta S)_l + R \ln \frac{x}{1-x}\right\} dx, \quad (11)$$

and ΔS_m has the maximum under the condition

$$\ln \frac{x}{1-x} = -\frac{(\Delta S)_l}{R}. \quad (12)$$

Following Rapoport $(\Delta S)_l$'s for cesium and tellurium are -1.0 cal/deg.mole and 0.154 cal/deg.mole respectively⁹. Substituting these values into eq.(11), the compositions x_s , corresponding to the maxima of the entropy changes during melting, are determined. And we can derive the pressures, at which entropy changes of melting show the maxima, as about 30 Kb for cesium and about 5 Kb for tellurium respectively.

These values may be verified by the observations of the latent heats of fusion under high pressure. However the experiments are not easy.

Pressure and Temperature Dependences of the Electrical Resistance of Bismuth

The transition curves of bismuth have been confirmed by many investigators and the correct phase diagram has been obtained. It is shown on Fig. 3¹⁴. However the crystal structures of high pressure phases are not yet determined. The bismuth I lattice can be described in two ways, as a lattice in which the rhombohedral angle is nearly 90° , the unit cell containing eight atoms, or as a rhomboheral lattice with an angle α which is nearly 60° , the unit cell containing two atoms. The atoms are arranged in double layers, each atom having three near neighbors in the double layer in which it is situated, and three others at a greater distance in an adjacent layer¹⁵. The bismuth II lattice is presumed as a body center cubic like structure¹⁶ or a hexagonal structure¹⁷. The higher pressure phases are not yet known.

On the other hand in liquid bismuth at atmospheric pressure there are about eight nearneighbors¹⁸. The volume change during melting is negative in bismuth I region.

The electric resistance of the liquid bismuth up to 12 kb has been observed in detail by Bridgman¹⁹, but the values at higher pressure had not been observed.

We observed them up to 280°C and 30 kb. The electric resistance of the liquid bismuth showed the characteristic change in the pressure range from

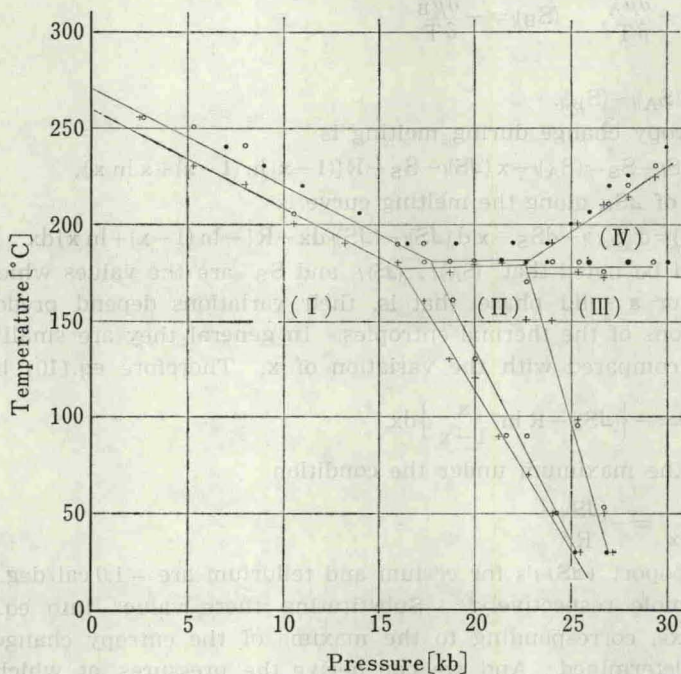


Fig. 3. The phase diagram of bismuth: observed by Jayaraman et al. •; observed in typical 2 runs in our experiments —, 0, +.

15 kb to 25 kb.

High pressure was induced by the usual piston-cylinder devices. A sample bismuth was heated by a cylindrical graphite tube set in talc, a pressure transmitting medium. Temperature was measured by the thermocouple of chromel-alumel, but the pressure effect on its thermoelectric force was neglected. The sample bismuth (prepared by Mitsubishi Kinzoku Kogyo Co., Ltd.) had a purity of 99.999% and the impurities were Au, Ag, Cu, Pb, Fe, Sb and As.

Fig. 4 shows the whole sample assembly and Fig. 5(a), 5(b) and 5(c) show the detailed arrangement of the sample holder. The hole, into which the bismuth was inserted, was drilled by the drill of 0.3 mm diam.. The bismuth was made as follows. A grain of the bismuth is put in a glass tube, the glass tube is heated until it becomes soft and then drawn in opposite directions in such a manner as the molten bismuth is drawn simultaneously. We can get a bismuth wire of an desired diameter in this manner. We neglect the chemical reaction during this process. The silver chloride chip under the sample holder was set to protect the transformation of the sample holder. The pyrophyllite chip on the sample holder was set to protect the sample holder from thrust of the alumina tube. The iron wires of 0.3 mm diam., on the market were used as the leads.

It is ideal that the measurements of electrical resistances are made by the potentiometer method, but its application seems to be very difficult under high

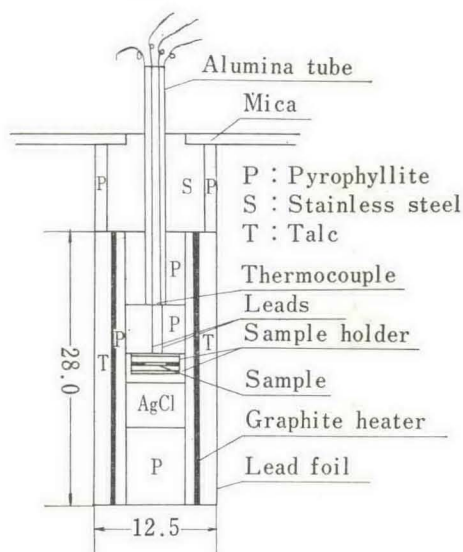


Fig. 4. The sample assembly.

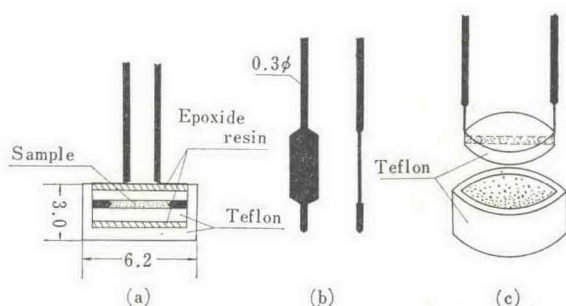


Fig. 5. The detailed representation of the sample holder.

pressure because of restriction of the sample assembly. The measurements then were made by the most primitive method (see Fig. 6). The amplifier of Ookura Denki Co., Ltd. and the two-pens recorder of Riken Denshi Co., Ltd. were used. The section surrounded by the dashed line in Fig. 6 shows the electrical circuit in the sample assembly.

The voltage V , detected on the recorder or the voltmeter, consists of the sum of the voltages due to the electrical resistances of the sample, the leads and the contacts (R_s , R_f and R_c respectively), and the thermoelectric force V_T . The sum of their electric resistances were 2 ohm at the highest. Therefore the current I was considered indeed constant within the limit of the effective number 3 in the whole pressure range in our experiments. The voltage V at given temperature and pressure then is written as

$$V = (R_s + R_f + R_c)I + V_T \quad (12)$$

Under atmospheric pressure, R_c is observable but never under high pressure,

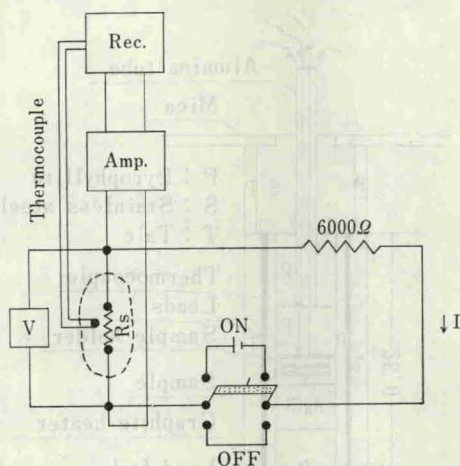


Fig. 6. The circuit observe the electrical resistances of bismuth.

because of restriction of the sample assembly. In the measurement of V in each run, however we had fused the bismuth at first and then cooled it to be solidified before measurement. Consequently R_c may be negligible compared with R_s and R_f . Eq.(12) then becomes

$$V = (R_s + R_f)I + V_T. \quad (13)$$

When the on-off switch is "off", V shows V_T only as we see in Fig. 6. Hence the difference of V 's in "on" and "off" gives the voltage $(R_s + R_f)I$. If $R_f I$ has been observed in advance in this manner, we can obtain $R_s I$, that is, R_s . But the observed values of $R_s I$'s were slightly scattered in every run, hence, the observed values of R_s 's were modified so as to give the correct R_s at atmospheric pressure^{19) 20) 21)}. The electrical resistances of the solid bismuth as functions of pressure and temperature were observed in this manner up to 30 kb and 150°C.

We shall explain in more detail about the measurement of the electric resistances of the liquid bismuth. It must be always required to inspect leaks of the liquid bismuth in the sample holder. We could not find the leaks out of the sample holder once after every run. However the penetrations of the liquid bismuth into the contacting faces of the leads and the hole in the sample holder are considered likely under high pressure, and if this penetrations take place, the observed values become higher. The effects of the penetrations are considerable, in the case that the variation of the electric resistance of the sample and the quantity of the sample are small. Therefore, if the penetrations have taken place, we must modify the directly observed values to obtain the quantitative values. In our experiments, the inspections of the penetrations and the modifications were made as follows. Under a given pressure, we rise temperature and observe the voltages at 50, 100, 150, 200, 250 and 280°C, we then lower temperature and observe the voltages again at the same temperatures.

If the penetrations have occurred during this cycle, the later are higher than the former at the corresponding temperatures. On the other hand we

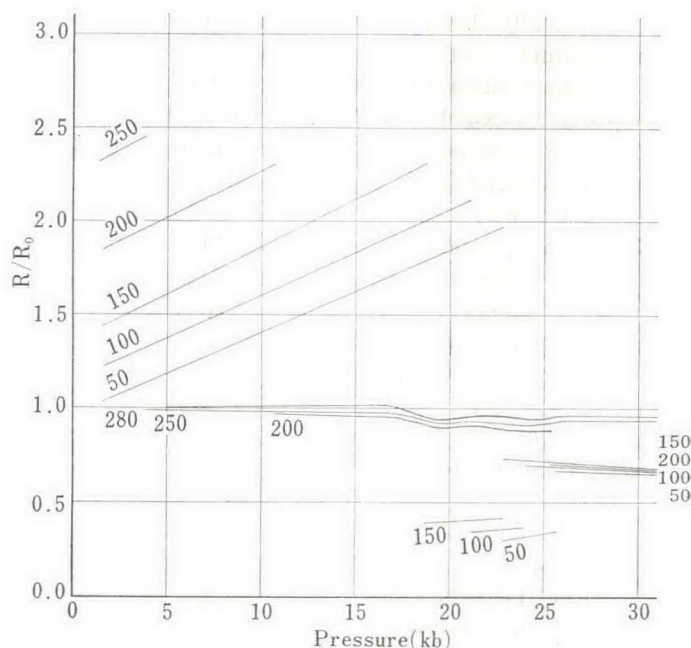


Fig. 7. The electrical resistances of bismuth as functions of pressure and temperature in terms of that at room temperature and 2.5 kb, R_0 as unity.

have already observed the electrical resistances of the solid bismuth up to 30 kb and 150°C. We need not have considered the effects of the penetrations in this case and have the correct values. Therefore, comparing the observed values in these two cases (one is up to 150 and the other up to 280°C), we can modify the directly observed electric resistance of the liquid bismuth. However we abandoned the observed values of the runs in which the penetrations had been less than 15%. After all, we used the values in the 5 runs of about had been less than 15%. After all, we use the values in the 5 runs of about 40 runs to arrange the experimental results. Fig. 7 shows the results obtained in such a manner as described above. The values of the electrical resistances in terms of that at room temperature and 2.5 kb as unity are given in Fig. 7.

The characteristic change in the pressure range from 15 kb to 25 kb seems to be due to the solid phases and to support the Rapoport's view. The values obtained in our experiments were slightly higher than those of Bridgman¹⁹⁾. But this may be due to the difference of experimental assemblies, in fact, the sample holders were extended in the radial direction by about 0.1 mm after every run.

The two species model is rather vague in its physical meanings. In fact, Rapoport himself had used such words as "in the broad sense of the word" in the definition of the model. Moreover, if a species is defined as Rapoport said, there are no pairs of different ions in the liquid and the quasichemical approach loses the physical meanings for the liquid. Nevertheless the several phenomena under high pressure could be explained or derived successfully by

using the model. Especially the greatest success may be in the explanation of the melting curves maxima. In the case of bismuth, this simple model cannot be applied, because the phase diagram is too complicated, that is, more than two species may be required to explain the phenomena of bismuth under high pressure. However this is not a important fault of the model, because the important view of Rapoport is condensed as "a liquid consists of species". The observed values of the electrical resistances of bismuth seem to support the Rapoport's view and Further, if the predicted pressures (30 kb for cesium and 5 kb for tellurium) at which the maxima of the entropy changes of melting takes place will be verified by experiments, it may be concluded that the Rapoport's view has a certain essential truths for a liquid.

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Part II

In the previous report of the same title, we have calculated, on the basis of the two species model of Rapoport, the volume decreases of the liquid cesium and the liquid tellurium along their melting curves, the condition of a melting curve maximum, and the pressures at which the entropy changes during melting take maxima. But any criticisms have not been made to the two species model in that report. We shall re-examine the several assumptions of Rapoport in the present report. Then we shall determine the forms of the radial distribution function and the pair-potential corresponding to the two species model to satisfy the Rapoport's assumptions simultaneously.

The Assumptions of Rapoport for Molten Cesium

There are two main assumptions in Rapoport's^{1) 2)} report they are

i) the assumption for the electrical resistance

$$R = (1 - \chi) R_I + \chi R_{III},$$

ii) the assumption for the property of the liquid that "the liquid consists of two species, in the broad sense of the word, the one corresponding to the low pressure phase and the other to the high pressure phase. A species therefore is characterized by coordination number, nearest neighbor distance and bond type. The liquid is looked upon as a quasilattice with an average coordination number and can be treated by statistical mechanical methods by use of Bragg-Williams and Quasichemical approximations."

We think that there is an inconsistency in the assumption ii). If a species is defined as ii), the all ions must be equivalent to each other and there are not any pairs between different ions in the liquid, hence the quasichemical approach loses its physical meanings. In fact, there may not be any pairs between different ions in a liquid consisting of equivalent atoms. Nevertheless the treatments have given the good results. Therefore it may be concluded that even if the two species model is ambiguous and includes the inconsistency in the physical sense, it has the correctness as a result of the mathematical treatments.

Radial Distribution Function and Pair Potential

We shall derive the forms of the radial distribution function and the pair-potential corresponding to the two species model, on the basis of its correctness as the results.

At first we consider the equation

$$g(r) = \alpha g_{AA}(r) + \beta g_{BB}(r), \quad (1)$$

where $g(r)$ is the radial distribution function for the liquid under consideration which can be observed, $g_{AA}(r)$, $g_{BB}(r)$ and α , β are proper functions of distance r and proper coefficients respectively. It is obvious that the transformation such as (1) of $g(r)$ is always possible mathematically. But, here, we look at the eq.(1) in the physical sense. The eq.(1) means that the observed feature of the distribution of the ions (i.e.g) consists of the superposition of the two different features of the distributions of the ions (i.e. g_{AA} and g_{BB}). Of course

the all ions must be equivalent to each other and the eq. (1) satisfies this physical demand. Then we look upon anew g_{AA} , g_{BB} as the species A and B respectively.

Now we consider the corresponding form of the pair-potential. It should be noted that arbitral two ions in the liquid form the species A or the species B, that is, the correlation between the two ions is shown by g_{AA} or g_{BB} . Therefore it may be reasonable to consider that the pair-potential consists of two different features too and the number of the features is restricted to two. The form of the pair-potential is then

$$\phi(r) = \alpha \phi_{AA}(r) + \beta \phi_{BB}(r), \quad (2)$$

$\phi(r)$ is the total pair-potential, ϕ_{AA} and ϕ_{BB} are corresponding to the species A and B respectively. It has not been established that the approximation by a pair-potential is reasonable for molten metal, but we proceed our discussion under the assumption that the approximation is reasonable.

Verification of Rapoport's Treatments

Ziman³⁾ has given an electrical resistivity of molten metal by

$$\rho = \frac{m v_F}{n e^2 \Lambda}, \quad (3)$$

Hereafter we use the notations of Ziman. The mean free path Λ of an electron in the liquid is written from Born approximation as

$$\frac{1}{\Lambda} = \frac{3\pi \epsilon_F^{1/2}}{2\sqrt{2}} \cdot \frac{\langle a \rangle \cdot |u|}{\epsilon_F^2}, \quad (4)$$

where

$$\langle a \rangle |u|^2 = \frac{1}{4k_F^4} \int_0^{2k_F} |u|^2 a(k) \cdot k^3 dk. \quad (5)$$

U_K is the Fourier transform of the pseudo potential of an ion in the liquid and $a(k)$ is the Fourier transform of the radial distribution function. Since all ions are equivalent to each other, U_K is equivalent for all ions. $a(k)$ is written as

$$a(k) = 1 + \frac{N}{V} \int (g-1) \frac{\sin kr}{kr} 4\pi r^2 dr. \quad (6)$$

Substituting the eq.(1) into the eq.(6) and pursuing the eq.'s (6), (5), (4) and (3) in this order, we have

$$\rho = \alpha \rho_{AA} + \beta \rho_{BB} \quad (7)$$

where

$$\rho_{AA} = \frac{m v_F}{n e^2 \Lambda_A},$$

$$\frac{1}{\Lambda_A} = \frac{3\pi \epsilon_F^{1/2}}{2\sqrt{2}} \cdot \frac{\langle a_{AA} \rangle |u|^2}{\epsilon_F^2},$$

$$\langle a_{AA} \rangle |u|^2 = \frac{1}{4k_F^4} \int_0^{2k_F} |u_k|^2 a_{AA}(k) \cdot k^3 dk,$$

and

$$a_{AA}(k) = 1 + \frac{N}{V} \int (g_{AA} - 1) \cdot \frac{\sin kr}{kr} 4\pi r^2 dr.$$

ρ_{BB} is given similarly. The eq.(7) corresponds to Rapoport's assumption i).

Therefore the assumption i) is reasonable for the liquid such as the valence electrons can be looked upon as free electrons and Born approximation is held.

Now we verify the quasichemical approach by using the eq.'s (1) and (2). The internal energy of the liquid is

$$E = \frac{N^2}{2V} \int \phi(r) \cdot g(r) 4\pi r^2 dr. \quad (8)$$

Here, the kinetic term is omitted, because this term is not affected by "species". Substituting the eq.'s(1) and (2) into the eq.(8), we have

$$E = \alpha^2 U_A + \beta^2 U_B + \alpha \cdot \beta \omega_{AB}, \quad (9)$$

where

$$\begin{aligned} U_A &= \frac{N^2}{2V} \int \phi_{AA} \cdot g_{AA} \cdot 4\pi r^2 dr, \\ U_B &= \frac{N^2}{2V} \int \phi_{BB} \cdot g_{BB} \cdot 4\pi r^2 dr, \\ \omega_{AB} &= \frac{N^2}{2V} \int (\phi_{AA} \cdot g_{BB} + \phi_{BB} \cdot g_{AA}) \cdot 4\pi r^2 dr. \end{aligned} \quad (10)$$

The internal energy E is the averaged value of those for all configurations of the whole ions. We have defined a species anew by using the corresponding radial distribution function in the last section, that is, the radial distribution function g_{AA} , g_{BB} are looked upon as the species A and B respectively. If we choose the coefficients α , β such as to satisfy $\alpha + \beta = 1$, α and β must show the mole fractions of the species A and B respectively.

Otherwise this means that the numbers of ions constituting the species A and B are αN and βN respectively. Moreover the eq.(1) must hold independently of an arbitrarily chosen origin ion. Hence the number of different configurations of the whole ions must be $N!/(\alpha N)! \cdot (\beta N)!$. The energy E is the averaged value for all configurations of $N!/(\alpha N)! \cdot (\beta N)!$. Therefore the partition function is given approximately by and the Helmholtz free energy is

$$Z_N = \frac{N!}{(\alpha N)! (\beta N)!} e^{-E/kT}, \quad (\alpha + \beta = 1)$$

$$F = E + N k T \{ \alpha \ln \alpha + \beta \ln \beta \}. \quad (11)$$

Substituting the eq.(9) into (11), we obtain the equilibrium condition

$$\Delta \mu^\circ = k T \ln \frac{\beta}{\alpha} + (\alpha - \beta) \omega = k T \ln \frac{x}{1-x} + (1-2x) \omega \quad (12)$$

where

$$\begin{aligned} \Delta \mu^\circ &= \mu_A^\circ - \mu_B^\circ, \\ \mu_A^\circ &= U_A/N, \quad \mu_B^\circ = U_B/N \\ \omega &= (\omega_{AB} - U_A - U_B)/N, \end{aligned}$$

and x is the mole fraction of the species B. The eq.(12) has the same form that Rapoport derive, and the assumption ii) is verified.

General Treatment of Species

The intensity of the diffracted x-ray or neutron-ray for the liquid described until in the last section is given by

$$a(k) = 1 + \frac{N}{V} \alpha \int (g_{AA} - 1) \cdot \frac{\sin kr}{kr} 4\pi r^2 dr + \frac{N}{V} \beta \int (g_{BB} - 1) \cdot \frac{\sin kr}{kr} 4\pi r^2 dr \quad (\alpha + \beta = 1) \quad (13)$$

There, we have treated the liquid as the species A and B are clearly distinguishable. In the present section, we treat such a liquid in which a difference between the species A and B is not so clear, that is, some ions belong to the species A and B simultaneously. If there are N_C ions belonging to the species A and B simultaneously, the numbers of ions constituting the species A and B clearly become $\alpha N - N_C/2$ and $\beta N - N_C/2$ respectively. The eq.(13) then becomes

$$N a(k) = \left[N + \frac{N}{V} N_A a_{AA}(k) + \frac{N}{V} N_B a_{BB}(k) + \frac{1}{V} \left(N_C + N_A \cdot \frac{a_{AA}(k)}{a_{CC}(k)} + N_B \cdot \frac{a_{BB}(k)}{a_{CC}(k)} \right) \cdot N_C \cdot a_{CC}(k) \right] \quad (14)$$

where

$$N_A = \alpha N - \frac{N_C}{2}, \quad N_B = \beta N - \frac{N_C}{2}$$

and $a_{AA}(k)$ is defined as same as in the last section. Others defined similarly. The configurational entropy becomes approximately

$$S = k \ln \frac{N!}{N_A! N_B! N_C!} = -k \left(N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N} + N_C \ln \frac{N_C}{N} \right) \quad (15)$$

for the same reason that has been said in the last section. As the number of the ions belonging to the species A and B simultaneously (i.e. N_C) increases, the eq.(14) becomes

$$a(k) \longrightarrow 1 + \frac{N}{V} a_{CC}(k)$$

and the eq.(15) becomes

$$S \longrightarrow 0$$

On the other hand, as the number of the ions decreases, $a(k)$ of the eq.(14) becomes that of the eq.(13) and the liquid in the present section becomes that in the last section.

Discussion

We have restricted the number of species to two, but the same treatment can be applied to a liquid consisting of more than two species. The forms of the radial distribution function and the pair-potential in this case become

$$g = \sum C_i g_{ii}$$

and

$$\phi = \sum C_i \phi_{ii}$$

C_i is the mole fraction of the species i and the sum is taken over all species which have influences to the properties of the liquid.

A species has a certain relation with the corresponding solid phase, but species corresponding to different solid phases are not always distinguishable. If distinguishable species exist in a molten metal, the influences must appear

in the entropy change during melting, as we see in our previous report. On the other hand, if species corresponding to different solid phases are not distinguishable, the influences do not appear, as we see in the last section. The problem of the distinguishability of species is complicated and does not yet solved, but we can conclude, on the basis of the results of the two species model, that species corresponding to solid phases such as the difference of the volumes is considerably large are distinguishable. An entropy change during melting and the distinguishability of species, of course, are not the problem concerning only to the difference of the volumes of the corresponding solid phases. In fact, an entropy change during melting of a semiconductor such as germanium or silicon is exceedingly large. And we cannot explain this fact by using only the concept of species. We must consider the states of the valence electrons too in this case. To solve these problems, of course we must clarify the relation between a species and the corresponding solid phase. However there are too little data to proceed our discussion actively.

References

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