Partial Structure Factors of Liquid Na—K and Al—Mg Alloys

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(Z. Naturforsch. **28 a**, 1002—1008 [1973] ; received 12 December 1972)

Three partial structure factors $S_{ij}(Q)$ have been evaluated from the scattered X-ray intensities of liquid Na—K and Al—Mg alloys assuming that the $S_{ij}(Q)$ are independent of the relative abundance of the respective elements in the alloys. The functions $S_{ii}(Q)$ and $S_{jj}(Q)$ and the reduced radial distribution functions $G_{ii}(r)$ and $G_{jj}(r)$ obtained in this work are very similar to those observed in the respective pure liquid metals. In both cases, $S_{ij}(Q)$ and $G_{ij}(r)$ have maxima which lie in between those of the pure elements. From these results, liquid Na—K and Al—Mg alloys are interpreted as random mixing fluids.

A comparison between the partial structure factors obtained in this work and those calculated from the hard sphere model was made. Adequate agreement was obtained on the low angle side of the first peak, but agreement on the whole pattern is not necessarily found. The electrical resistivity was calculated using Faber-Ziman's theory and compared with experimental data.

1. Introduction

During the recent progress in the theory of liquid binary alloys the importance of the three partial distribution functions of the atoms has been emphasized. By Fourier transformation of the X-ray scattering intensity for liquid binary alloys alone, however, these three functions cannot be easily determined as one needs the information of three independent scattering experiments. Keating[1] suggested that in principle the three partial structure factors $[S_{ij}(Q), i, j = 1, 2]$ can be obtained by diffraction experiments. The first attempt of this kind was performed by Enderby, North and Egelstaff[2] in a neutron diffraction investigation of liquid Cu_6Sn_5 alloys in which the scattering power of Cu was varied by using different Cu-isotopes. From the obtained $S_{ij}(Q)$, they were able to predict the diffraction pattern of a Cu-Sn alloy of a different concentration which was in good agreement with the experimentally observed X-ray data. Besides, they showed that $S_{ii}(Q)$ and $S_{jj}(Q)$ were very similar to the structure factors of the pure components. These results seem to indicate that the $S_{ij}(Q)$ are practically independent of the composition.

With reference to these results, in a work concerning the liquid system Ag-Sn, Halder and Wagner[3] assumed that the partial structure factors were independent of the composition and $S_{\mathrm{Ag-Sn}}(Q)$ was calculated from X-ray diffraction patterns at several compositions. The resultant $S_{\mathrm{Ag-Ag}}(Q)$ and $S_{\mathrm{Sn-Sn}}(Q)$ were again found to be very similar to the structure factors of the respective pure liquids and the partial structure factors observed in these liquid alloys suggested that the atomic distribution was not random as expected from the measurement of the electrical resistivity and magnetic susceptibility. Later, a similar behaviour was also found by their group in liquid Au – Sn[4] and Cu – Sn[5].

Isherwood and Orton[6] calculated $S_{ij}(Q)$ for liquid Bi – In alloys with the following two assumptions: the partial structure factors are independent of the composition and the $S_{ii}(Q)$ are the same as in the pure liquids. However, a comparison of the $S_{ij}(Q)$ obtained by the two methods mentioned above has not been reported.

The hard sphere model[7–9] gives directly the partial structure factors in terms of the assumed hard sphere diameters, and it is found that this model is useful for the calculation of the electrical resistivity of binary liquid alloys using Faber-Ziman's theory[10]. The calculated structure factors do not show appreciable dependence on concentration. Besides, the peak maximum of $S_{ij}(Q)$ falls roughly into the middle between the maxima of $S_{ii}(Q)$ and $S_{jj}(Q)$. In the works of Wagner et al.[3–5], the maximum of $S_{ij}(Q)$ falls between the maxima of $S_{ii}(Q)$ and $S_{jj}(Q)$, but not exactly into the middle. Thus the hard sphere mixture model

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seems to be appropriate for binary liquid alloys interpreted as random mixing fluids.

The purpose of this work is to determine the partial structure factors and to compare the atomic distributions obtained by the methods of Wagner et al. and of Isherwood and Orton. We chose the systems Al – Mg and Na – K because not only the analysis has not yet been performed but also random mixing is expected from several observed properties, for the example electrical resistivity and the heat of mixing. Besides, a comparison is made between the structure factors obtained from diffraction data and those calculated by the hard sphere model[7–9]. Electrical resistivities calculated with the obtained three partial structure factors from diffraction data using Faber-Ziman's theory[10], are compared with experimental data.

2. Evaluation of Partial Structure Factors and Atomic Distribution Functions

For a binary alloy the relation between the total structure factor $S(Q)$ directly obtained by X-ray diffraction experiments and the three partial structure factors $S_{ij}(Q)$ is

$$S(Q) = \left[\frac{c_i^2 f_i^2}{\langle f\rangle^2}\right] S_{ii}(Q) + \left[\frac{c_j^2 f_j^2}{\langle f\rangle^2}\right] S_{jj}(Q) + \left[\frac{2\,c_i c_j f_i f_j}{\langle f\rangle^2}\right] S_{ij}(Q) \qquad (1)$$

with $Q = 4\pi \sin\theta/\lambda$, λ the wavelength, 2θ the scattering angle, $\langle f\rangle = \Sigma c_i f_i$, c_i and f_i the atomic fraction and the atomic scattering factor of the atomic species i.

In this work Eq. (1) was solved using the X-ray diffraction data from the work of Gingrich and Henderson[11] and Henninger et al.[12] for the Na – K system and those of Steeb and Woerner[13] for the Al – Mg system by the following two methods.

Method (A) – the method used by Wagner et al.[3–5]

Three partial structure factors are calculated from the total structure factors at several compositions by solving three simultaneous equations based on Equation (1).

Method (B) – the method used by Isherwood and Orton[6]

The partial structure factor $S_{ij}(Q)$ is calculated under the assumption that $S_{ii}(Q)$ and $S_{jj}(Q)$ are the same as in of the pure components.

In order to obtain the information on the detailed structure of the alloys, the partial radial distribution function $\varrho_{ij}(r)$ which is the Fourier transform of the partial structure factor $S_{ij}(Q)$ and indicates the number of j-type atoms per unit volume at a distance r from an i-type atom, is introduced. As pointed out by Halder and Wagner[3]

$$G_{ij}(r) = 4\pi r\varrho_0[\varrho_{ij}(r)/\varrho_j - 1] = \frac{2}{\pi}\int_0^\infty Q[S_{ij}(Q) - 1]\sin(Q\cdot r)\,dQ\,, \qquad (2)$$

with $G_{ij}(r)$ the partial reduced distribution function, $\varrho_j = c_j\varrho_0$ and ϱ_0 the average atomic density. The three pair distribution functions ($i - i$, $j - j$ and $i - j$) are directly obtained by Eq. (2) from the partial structure factors.

The numerical calculation was performed on the NEAC-2200, Model-700 in the Computer Centre, Tohoku University.

3. Results and Discussion

3.1. Partial structure factors and distribution functions

Figures 1 and 2 show the partial structure factors obtained for the liquid Na – K and Al – Mg systems. As shown in these figures, $S_{\text{Na-Na}}(Q)$, $S_{\text{K-K}}(Q)$, $S_{\text{Al-Al}}(Q)$ and $S_{\text{Mg-Mg}}(Q)$ calculated the method (A) closely resemble the structure factors of the pure liquid metals[14–16]. This seems to indicate that the partial structure factors are independent of the composition in these liquid alloys.

The calculation was performed on two sets of data (Al – 11, 27, 42.5 at-% Mg; Al – 39.5, 52.6, 62.5 at-% Mg) for the Al – Mg system. The information obtained from different combinations of the data was quite similar. For the Na – K system available data of X-ray diffraction are limited. Hence, the calculation was done on one set of the data (Na – 21.6, 50.0, 87.8 at-% K). Figure 3 shows the results for the Na – K system obtained by method (B). The partial structure factors $S_{\text{Na-K}}(Q)$, derived from the total structure factors for different concentrations, are in general similar to one another. For the Al – Mg system a similar behaviour is found.

The peak positions of the partial structure factors together with those found in the pure liquid metals[14–16] are summarized in Table 1. It is found that the positions of the peak maxima of $S_{ij}(Q)$ in

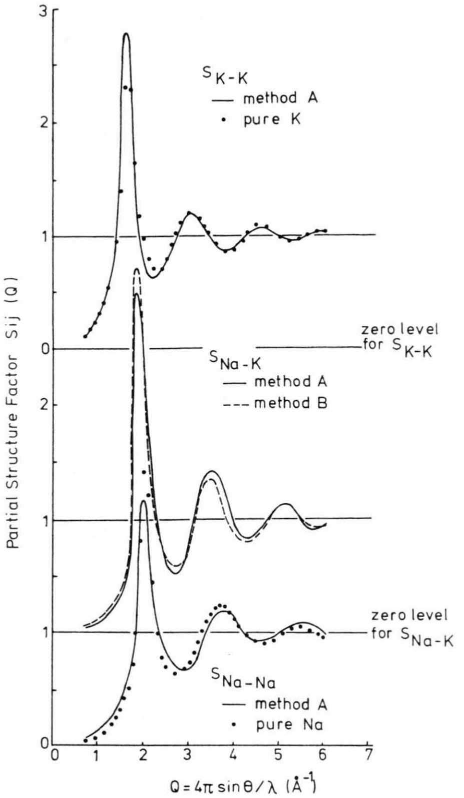

Fig. 1. Three partial structure factors of the liquid Na—K system calculated from the experimental data [11, 12].

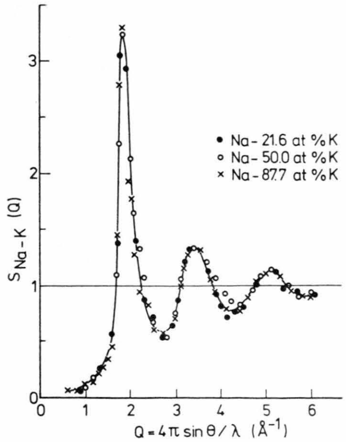

Fig. 3. Partial structure factor of the different atom pairs, $S_{Na-K}(Q)$.

both systems fall well into the middle between those of $S_{ii}(Q)$ and $S_{jj}(Q)$. The total structure factors obtained by X-ray diffraction for these systems show no anomalies at any particular composition. Hence these results suggest that the structures of the

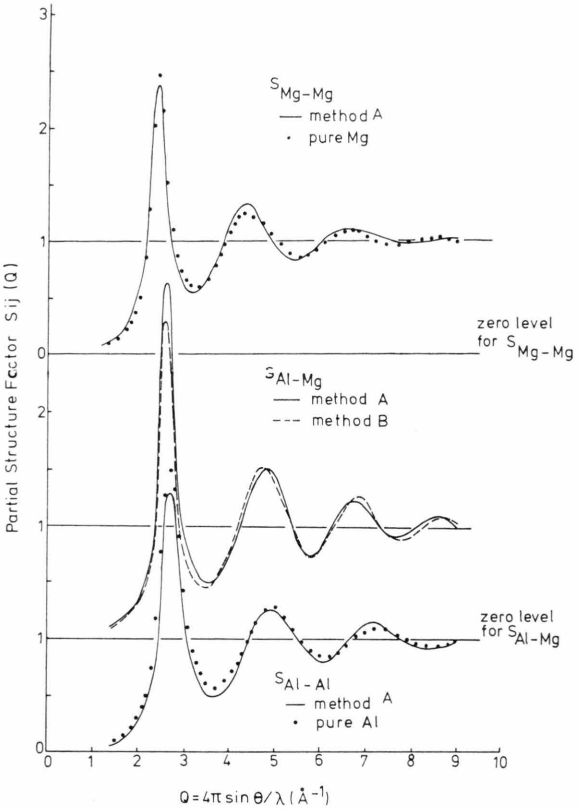

Fig. 2. Three partial structure factors of the liquid Al—Mg system calculated from the experimental data [13].

crystalline compounds, for example NaK, NaK_2 [17]; Al_3Mg_2 [18], do not influence the liquid structure.

In order to clarify this point the partial distribution functions were derived. Figures 4 and 5 show the partial reduced distribution functions calculated from $S_{ij}(Q)$ using Eq. (2) for alloys from the systems Na—K and Al—Mg. Again, $G_{ii}(r)$ and $G_{jj}(r)$ look similar to those observed in the corresponding pure liquid metals.

As is well-known, the area under the first peak in the radial distribution function gives the coordination number of nearest neighbour atoms and the position of the first peak maximum gives the interatomic distance of nearest nighbours. The positions of the peak maxima of $G_{ij}(r)$, the interatomic distance r_1 and the coordination number of nearest neighbour atoms n_1 obtained in this work are listed in Table 2.

In the Na—K system a Na—Na interatomic distance $r_1 = 3.80$ Å and a K—K interatomic distance $r_1 = 4.67$ Å is observed, in good agreement

Table 1. Partial structure factors calculated from the experimental data [11–13].

	pure Na	$S_{\mathrm{Na-Na}}$ (A)	$S_{\mathrm{Na-K}}$ (A)	$S_{\mathrm{Na-K}}$ (B)	$S_{\mathrm{K-K}}$ (A)	pure K	mean position
1st max	2.02	2.00	1.83	1.83	1.63	1.63	1.83
1st min	2.75	2.85	2.68	2.70	2.20	2.28	2.52
2nd max	3.72	3.76	3.50	3.47	3.04	3.02	3.37
2nd min	4.70	4.62	4.30	4.25	3.80	3.90	4.30
	pure Al	$S_{\mathrm{Al-Al}}$ (A)	$S_{\mathrm{Al-Mg}}$ (A)	$S_{\mathrm{Al-Mg}}$ (B)	$S_{\mathrm{Mg-Mg}}$ (A)	pure Mg	mean position
1st max	2.68	2.70	2.55	2.55	2.41	2.43	2.56
1st min	3.70	3.70	3.50	3.48	3.15	3.25	3.48
2nd max	4.96	4.95	4.75	4.65	4.30	4.23	4.60
2nd min	6.15	6.10	5.82	5.73	5.40	5.57	5.86

Peak positions are represented in Å^{-1}, (A) and (B) denote the results obtained by the method (A) and (B) respectively. Mean position $= \frac{1}{2}(S_{i\text{-pure}}+S_{j\text{-pure}})$.

with the values observed in the respective pure liquid metals, whereas the observed Na—K interatomic distance $r_1 = 4.21$ Å [method (A)] or $r_1 = 4.18$ Å [method (B)] is very close to the mean value $r_{\text{mean}} = 4.23$ Å of the Na—Na and K—K interatomic distances. As shown in Table 2, the same is also true for the Al—Mg system. The coordination number of the different atom pairs (Na—K and Al—Mg) is in moderate agreement with the mean value between those of identical atom pairs. These results support the conclusion of the early works on total structure factors [11, 13]. From the results obtained so far, liquid Na—K and Al—Mg alloys random mixing fluids and there is no evidence for a tendency of compound formation in these liquid binary alloys [17, 18]. On the other hand, the partial structure factors $S_{ij}(Q)$ calculated by different methods [(A) or (B)] are quite similar. This indicates the applicability of the assumption used in the method (B) for the derivation of $S_{ij}(Q)$, as was also pointed out in our previous work for Hg—In and Hg—Tl systems [19].

As mentioned in the introduction, Ashcroft and Langreth [7] and Enderby and North [8] independently suggested to apply the Fourier transforms of the hard sphere solutions of the Percus-Yevick equation on binary mixtures. In terms of the Ornstein-Zernike direct correlation functions $C_{ij}(Q)$ the partial

Table 2. Partial distribution functions calculated from the partial structure factors of Table 1.

	pure Na	$G_{\mathrm{Na-Na}}$ (A)	$G_{\mathrm{Na-K}}$ (A)	$G_{\mathrm{Na-K}}$ (B)	$G_{\mathrm{K-K}}$ (A)	pure K	mean value
1st max	3.75	3.74	4.10	4.08	4.56	4.58	4.17
1st min	5.32	5.22	5.81	5.70	6.40	6.42	5.87
2nd max	7.03	7.05	7.50	7.53	8.58	8.50	7.77
2nd min	8.52	8.67	9.20	9.16	10.4	10.4	9.45
r_1	3.82	3.80	4.21	4.18	4.67	4.64	4.23
n_1	9.8	9.6	9.8	10.1	9.6	9.5	9.7
	pure Al	$G_{\mathrm{Al-Al}}$ (A)	$G_{\mathrm{Al-Mg}}$ (B)	$G_{\mathrm{Al-Mg}}$ (B)	$G_{\mathrm{Mg-Mg}}$ (A)	pure Mg	mean value
1st max	2.80	2.82	3.02	3.01	3.18	3.17	2.99
1st min	3.90	3.82	4.21	4.27	4.83	4.88	4.39
2nd max	5.08	5.13	5.40	5.46	5.95	5.93	5.51
2nd min	6.22	6.27	6.63	6.68	7.16	7.16	6.69
r_1	2.82	2.84	3.04	3.02	3.23	3.20	3.01
n_1	11.5	11.3	10.8	10.5	10.6	10.4	11.0

Peak positions are represented in Å, (A) and (B) denote the results obtained by the method (A) and (B) respectively, r_1 is the nearest neighbour distance, and n_1 ist the 1st coordination number of atoms, mean value $= \frac{1}{2}(G_{i\text{-pure}}+G_{j\text{-pure}})$.

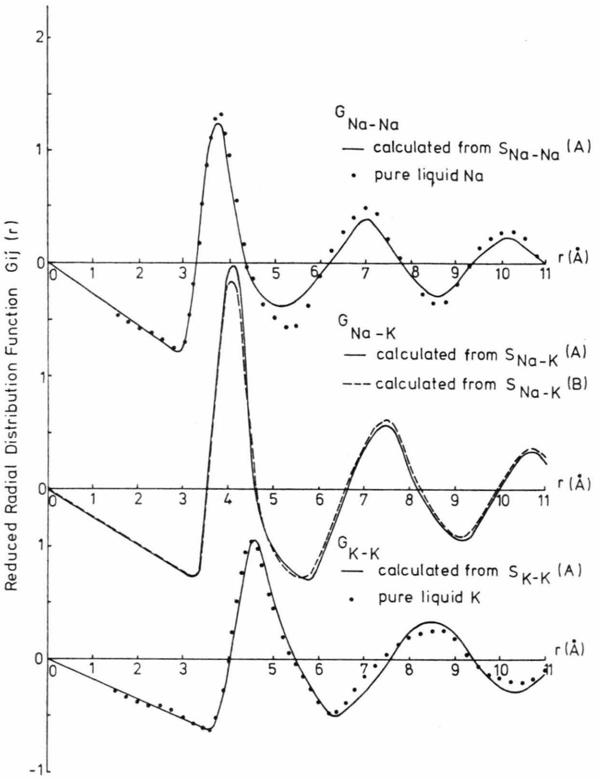

Fig. 4. Three partial reduced distribution functions of the liquid Na—K system.

structure factors in this model are

$$a_{ii}(Q) = [1 - \varrho_j C_{jj}(Q)]/D(Q), \tag{3}$$

$$a_{jj}(Q) = [1 - \varrho_i C_{ii}(Q)]/D(Q), \tag{4}$$

$$a_{ij}(Q) = (\varrho_i \varrho_j)^{1/2} C_{ij}(Q)/D(Q), \tag{5}$$

$$D(Q) = [1 - \varrho_i C_{ii}(Q)][1 - \varrho_j C_{jj}(Q)] - - \varrho_i \varrho_j [C_{ij}(Q)]^2 \tag{6}$$

with ϱ_j the number density of the j-component. The following conversion is required to perform a practical comparison of the partial structure factors observed with those calculated from the hard sphere model:

$$S_{ij}(Q) = (\varrho_i \varrho_j)^{-1/2} [a_{ij}(Q) - \delta_{ij}] + 1 \tag{7}$$

(δ_{ij} is the Kronecker symbol).

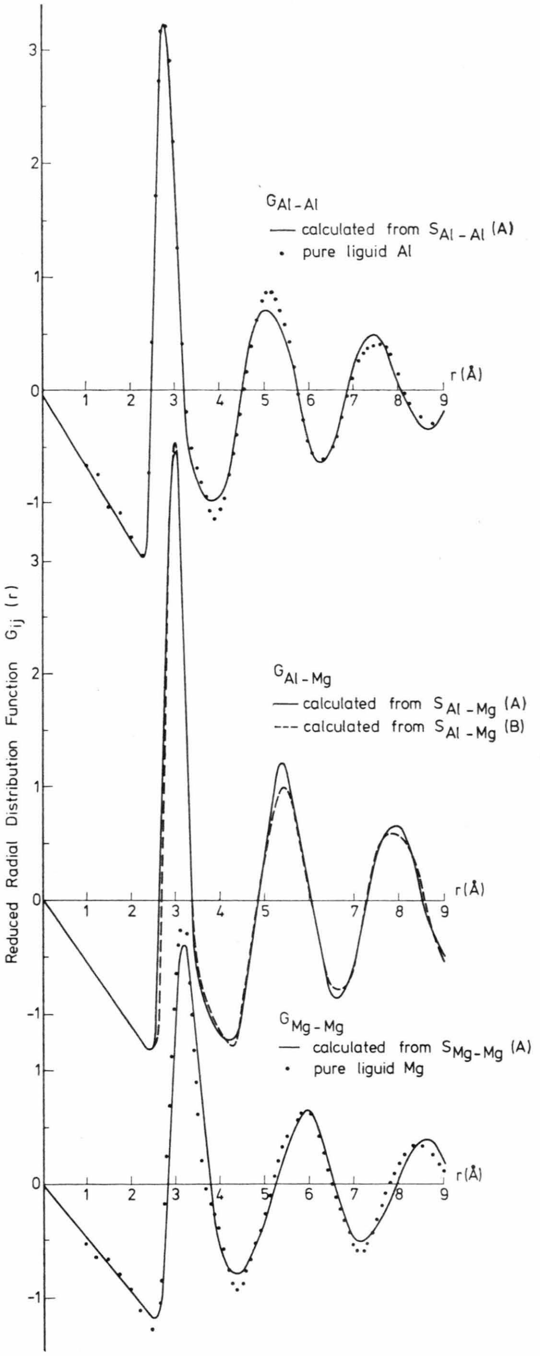

Fig. 5. Three partial reduced distribution functions of the liquid Al—Mg system.

Waseda and Suzuki[20] showed that the hard sphere diameter (σ) for one component liquid metals is close to the distance (r_0) of the first node in the effective interionic pair potential. Using the density for liquid Na—K and Al—Mg allows obtained experimentally[21, 22] and the assumption $\sigma = r_0$, the total packing fraction became 0.44 ± 0.02 in both systems. This is in good agreement with the value (0.45) used by Ashcroft and Langreth[7]. We have calculated the partial structure factors in the hard sphere model for 1 : 1 mixtures using Eq. (3) ~ (7) with $\sigma(\text{Å}) = 3.25$, 4.10, 2.50 and 2.70 for Na, K, Al and Mg respectively and the total packing fraction 0.45.

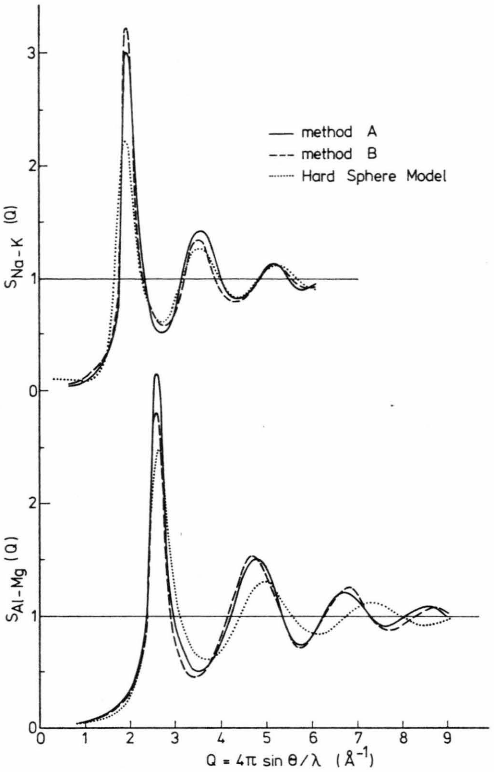

Fig. 6. A comparison between $S_{ij}(Q)$ derived from the experimental data and calculated by the hard sphere mixture model.

Figure 6 shows of partial structure factors of the atom pairs $S_{ij}(Q)$ calculated according to method (A) and (B) and according to the hard sphere model. Adequate agreement is obtained on the low angle side of the first peak maximum, but in the region of higher Q-values the disagreement between the curves for method (A) and (B) and the hard sphere model is evident. In the electrical resistivity calculations, the structure factors in the range of Q from 0 to $2\,k_f$, where k_f is the Fermi wave vector, are used. The essential agreement of the electrical resistivity as observed and as calculated[7] with the hard sphere mixture model is only due to this part of the structural information. However, the hard sphere model can not express the detailed structure of liquid binary alloys as shown in Figure 6. It is found that the softness of the repulsive core in the effective interionic pair potentials for liquid metals is realistic, in contrast to rare-gas liquids[23]. Further precise experiments as suggested by Enderby et al.[2] and considerations including the softness of the repulsive core and subsequent long-range oscillatory characteristics of the effective interionic pair potential in liquid metals should be performed.

3.2. Electrical resistivity of liquid binary alloys

Ziman[24] showed that the electron transport properties in liquid metals depend on the structure factor $S(Q)$ and the pseudopotential matrix element $U(Q)$. Faber and Ziman[10] extended this approach to liquid binary alloys by means of the concept of the random substitutional model and the nearly free electron theory.

According to Faber-Ziman's theory[10], the electrical resistivity (ϱ) for a liquid binary alloy is given by

$$\varrho = \frac{12\,\pi}{e^2\,\hbar\,v_f^2\,\varrho_0} \int_0^1 |U(Q)|^2\,(Q/2\,k_f)^3\,\mathrm{d}(Q/2\,k_f), \tag{8}$$

$$|U(Q)|^2 = c_i\,c_j[U_i(Q) - U_j(Q)]^2 + \sum_{\alpha=i}^{j}\sum_{\beta=i}^{j} c_\alpha\,c_\beta\,U_\alpha(Q)\,U_\beta(Q)\,S_{\alpha\beta}(Q), \tag{9}$$

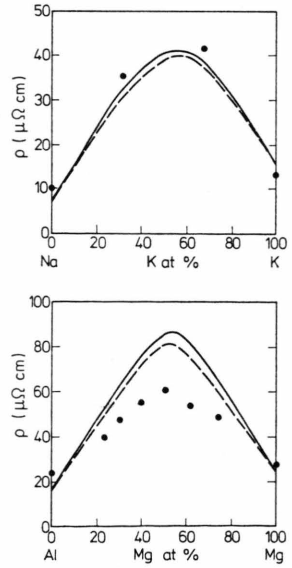

Fig. 7. Electrical resistivity of the liquid Na—K and Al—Mg system. The solid dots denote the experimental values (Na—K, at 100 °C[7]; Al—Mg, at 500 °C[13]). The solid and dashed lines denote the values calculated from $S_{ij}(Q)$ — (A) and $S_{ij}(Q)$ — (B) respectively.

with e the charge of an electron, v_f the Fermi velocity and k_f the Fermi wave vector.

Among the various pseudopotentials which represent the properties of the isolated ions apart from the screening effect of the conduction electrons[25], Shaw's model potential[26] is accepted to be a reasonable one, because in his model the selection of the parameter which is indispensable for Heine-Abarenkov's model potential[27], is not crucial. Only a few applications of this model potential are reported. Therefore, electrical resistivity calculations for liquid Na – K and Al – Mg alloys have been performed using the partial structure factors derived from the experimental data in this work and the pseudopotential matrix element suggested by Shaw[26].

As shown in Fig. 7 the predicted and experimental values agree reasonably well. For both systems, a 1 : 1 alloy yields a resistivity about two or three times larger than that of the pure components. The values calculated in this work represent this basic behaviour. But, as far as we know, experimental data on the electrical resistivity just above the liquidus temperature have not been reported. Therefore, detailed comments should await further experiments including the structural analysis for these systems as suggested by Keating[1] and Enderby, North, and Egelstaff[2].

Acknowledgements

The authors are grateful for useful discussions with the members of the Ohtani's Laboratory. We would also like to thank the Computer Centre, Tohoku University for allowing the use of their computer.

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