Atomic Distributions and Electrical Resistivities of Liquid Gold-Tin Alloys *

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The distributions $\varrho_{ij}(r)$ of Au-Au, Sn-Sn and Au-Sn pairs have been calculated using the three partial interference functions $I_{ij}(K)$ which were evaluated from the scattered x-ray intensities of liquid Au-Sn alloys measured by Kaplow, Strong and Averbach. The functions $I_{\mathrm{AuAu}}(K)$ and $I_{\mathrm{SnSn}}(K)$ and their corresponding Fourier transforms are similar to those observed in their respective pure liquids. The functions $I_{\mathrm{AuSn}}(K)$ and $\varrho_{\mathrm{AuSn}}(r)$ resemble closely a model structure based on a solid AuSn alloy with a NiAs-type structure. The electrical resistivities of the alloys obtained with $I_{ij}(K)$ and the pseudo-potential elements $U_i(K)$ show a large increase upon alloying Sn into Au in agreement with experimental observation.

The three partial interference functions $I_{ij}(K)$ (also called structure factors) which characterize the x-ray or neutron scattering of liquid binary[1] alloys have recently been determined for a Cu-45 at. % Sn alloy by ENDERBY, NORTH, and EGELSTAFF[2] employing neutron diffraction methods in which the scattering power of Cu was varied. From the observed $I_{ij}(K)$ they were able to predict the diffraction pattern of a Cu-Sn alloy of a different concentration which showed reasonable agreement with previous x-ray data[3]. Recent measurements in our laboratory produced very good agreement between predicted and experimental x-ray intensities for the liquid Cu-45 at. % Sn alloy[4]. This result seems to indicate that, to a good approximation, $I_{ij}(K)$ are independent of the relative abundance of the elements in these alloys.

Using the above assumption, HALDER and WAGNER[5] have successfully calculated $I_{ij}(K)$ of liquid Ag-Sn alloys from their x-ray scattering patterns. The partial functions due to the Ag-Ag pairs and Sn-Sn pairs closely resembled those of the corresponding pure elements whereas the positions of the peaks of the partial function due to Ag-Sn pairs lay in between those of the Ag-Ag and Sn-Sn functions, which is predicted by the hard sphere model[6, 7].

The x-ray scattering patterns of liquid Au-Sn alloys have been published recently by KAPLOW, STRONG and AVERBACH[8]. These authors concluded that the atomic distributions of the alloys are the sums of the distributions of AuSn and pure Au for alloys of less than 50 atomic per cent Sn concentrations and those of AuSn and pure Sn for higher Sn concentrations.

The neutron experiments would be difficult to apply to the Au-Sn system. An alternative approach is to evaluate the partial interference functions $I_{\mathrm{AuAu}}(K)$, $I_{\mathrm{SnSn}}(K)$ and $I_{\mathrm{AuSn}}(K)$, from the total interference function $I(K)$ of Au-Sn alloys obtained from the x-ray data of KAPLOW et al.[8], assuming that $I_{ij}(K)$ are independent of concentration. The purpose of this paper is to present (1) the partial atomic distribution functions $G_{ij}(r)$ which represent the Fourier transforms of $K[I_{ij}(K)-1]$, i. e., $G_{ij}(r)=\mathrm{transf}\{K[I_{ij}(K)-1]\}$ and the fit between the experimental, total

$$G(r)=\mathrm{transf}\{K[I(K)-1]\}$$

and those calculated from $G_{ij}(r)$, and (2) the variation of electrical resistivity ϱ_{R} in the alloy with concentration calculated with $I_{ij}(K)$ and the Fourier transforms $U_i(K)$ of the pseudopotentials.

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Partial Interference and Atomic Distribution Function

The total interference function $I(K)$ is defined as

$$I(K)=\{I_a(K)-[\langle f^2\rangle-\langle f\rangle^2]\}/\langle f\rangle^2,$$

where $I_a(K)$ is the elastically scattered radiation per atom in electron units, $\langle f\rangle$ and $\langle f\rangle^2$ are the mean and mean square scattering factors of the alloy. $I(K)$ can be written [1, 5, 10] as:

$$I(K)=w_{11}\,I_{11}(K)+w_{22}\,I_{22}(K)+2\,w_{12}\,I_{12}(K), \quad (1)$$

where $w_{ij}=c_i\,c_j\,f_i\,f_j/\langle f\rangle^2$, c_i and f_i being the concentration and atomic scattering factor of element i, respectively. $I_{ij}(K)$ is related to the atomic distribution function $\varrho_{ij}(r)$, which is equal to the number of j-type atoms per unit volume at a distance r from an i-type atom, i. e.,

$$I_{ij}(K)=1+\int_0^\infty 4\,\pi\,r^2\,\varrho_0[\varrho_{ij}/\varrho_j-1] \quad (2)$$
$$[(\sin K\,r)/(K\,r)]\;\mathrm{d}r,$$

where ϱ_0 is the average atomic density and $\varrho_j=\varrho_0\,c_j$.

For the analysis of $I_{ij}(K)$, the total $I(K)$ as shown in Fig. 1 were calculated from

$$F(K)=K[I(K)-1]$$

published by KAPLOW, STRONG and AVERBACH [8]. By the least square analysis of five $I(K)$ with different Sn concentrations, the best values of $I_{\mathrm{AuAu}}(K)$, $I_{\mathrm{SnSn}}(K)$ and $I_{\mathrm{AuSn}}(K)$ were obtained (Fig. 2). The root mean square deviation of each data point of $I_{ij}(K)$ was less than 0.1 in the region of the first peak which is probably within the accuracy of the experimental data, and less than 0.02 beyond $K=3.5$ Å^{-1}.

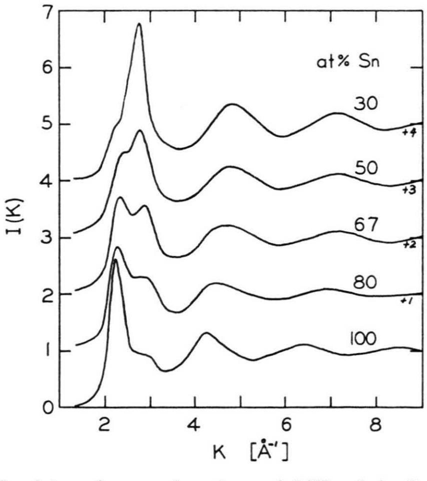

Fig. 1. Total interference functions of $I(K)$ of Au-Sn alloys, evaluated from $F(K)=K[I(K-1)]$ of KAPLOW, STRONG and AVERBACH [8].

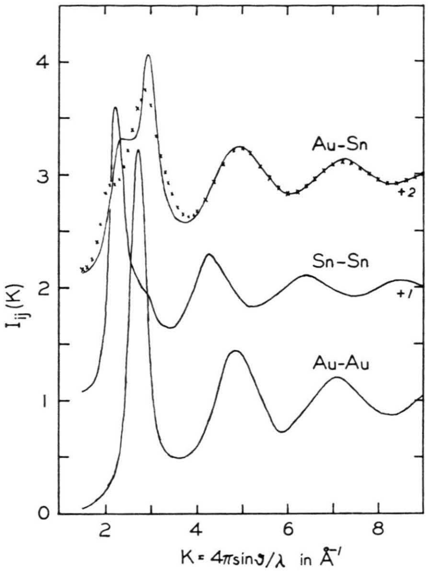

Fig. 2. Partial interference functions $I_{\mathrm{AuAu}}(\mathrm{K})$, $I_{\mathrm{SnSn}}(K)$ and $I_{\mathrm{AuSn}}(K)$ (solid curves) [9]. The curve represented by xxx corresponds to a model $I_{\mathrm{AuSn}}(K)$ based on a model structure proposed by KAPLOW, STRONG and AVERBACH [8].

The functions $I_{\mathrm{AuAu}}(K)$ and $I_{\mathrm{SnSn}}(K)$ closely resemble those of the pure liquids Au [11] and Sn [4, 8], respectively. $I_{\mathrm{AuSn}}(K)$ is similar to $I(K)$ of the pure AuSn alloy, but its maximum occurs at $K_1=2.94$ Å^{-1} which is larger than the positions $K_1=2.67$ Å^{-1} of pure Au and $K_1=2.78$ Å^{-1} of the AuSn alloy. In addition a subsidiary peak occurs below the first maximum. Such an interference function with the first peak maximum $K_1=2.90$ Å^{-1} can be obtained from an atomic distribution similar to an ordered AuSn alloy with NiAs-type structure as shown by KAPLOW et al. [8] (see Fig. 2).

The Fourier transform of $K[I_{ij}(K)-1]$ yields directly the partial atomic distribution function

$$G_{ij}(r)=4\,\pi\,r[\varrho_{ij}(r)/c_{ij}-\varrho_0] \quad (3)$$
$$=\frac{2}{\pi}\int K[I_{ij}(K)-1]\,\sin K\,r\,\mathrm{d}K,$$

which are shown in Fig. 3. Again $G_{\mathrm{AuAu}}(r)$ and $G_{\mathrm{SnSn}}(r)$ look similar to those observed in their

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corresponding pure liquids. From these patterns, a Au-Au interatomic distance $r_1 = 2.84$ Å and a Sn-Sn distance $r_1 = 3.16$ Å can be obtained which are identical to the values observed in the respective pure liquids [4, 8, 11], whereas $G_{\mathrm{AuSn}}(r)$ yields a Au-Sn distance $r_1 = 2.88$ Å which is very close to the value of $r_1 = 2.86$ Å found in solid AuSn.

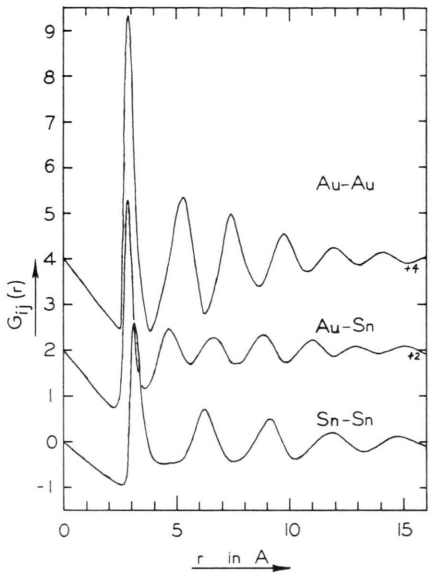

Fig. 3. Partial atomic functions $G_{ij}(r)$ obtained by Fourier transform of $K[I_{ij}(K-1)]$.

It is customary to calculate the Fourier transform of $K[I(\mathrm{K}) - 1]$, where $I(K)$ is the total interference function, which is called the total atomic distribution function $G(r)$, i. e.

$$G(r) = \frac{2}{\pi} \int K[I(\mathrm{K}) - 1] \sin K r \, \mathrm{d}K . \tag{4}$$

$G(r)$ is related to $G_{ij}(r)$ by the convolution integral:

$$\begin{aligned} G(r) &= \sum_{ij} W_{ij}(r) * G_{ij}(r) && (5) \\ &= \sum_{ij} \int W_{ij}(u) \, G_{ij}(u+r) \, \mathrm{d}u, \end{aligned}$$

where $W_{ij}(r)$ is the Fourier transform of w_{ij}, which is a very slowly varying function of K, and to a good approximation one may assume it to be independent of K. In the case of binary alloys one can write:

$$G(r) = w_{11} G_{11}(r) + w_{22} G_{22}(r) + 2 w_{12} G_{12}(r) . \tag{6}$$

The atomic distribution functions $G(r)$ are shown in Fig. 4. The solid curves represent the Fourier transforms of $K[I(K) - 1]$ [Eq. (4)] and the dotted curves $G(r)$ as calculated with Eq. (6) from the values of $G_{ij}(r)$. As can be seen, the agreement is reasonable.

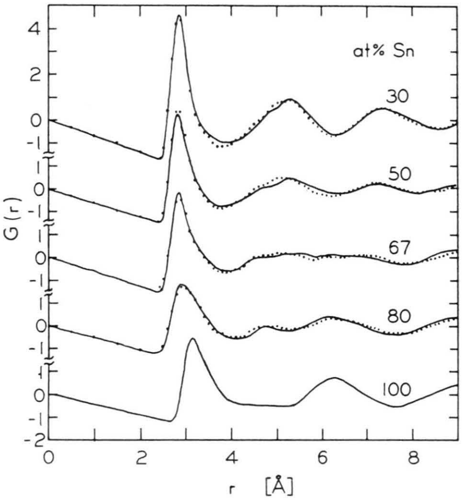

Fig. 4. Solid curves represent the total atomic distribution function $G(r) = \text{trans}\, F(K)$ of Au-Sn alloys. Dotted curves represent $G(r) = \sum_{i,j=1}^{2} w_{ij} \, G_{ij}(r)$.

Electrical Resistivity of the Alloys

A knowledge of $I_{ij}(K)$ allows us to evaluate the electrical resistivity ϱ_{R} of the liquid alloys. As shown be FABER and ZIMAN [12], the electrical resistivity ϱ_{R} is given by:

$$\varrho = [\pi^3 \hbar \, Z/(e^2 k_{\mathrm{F}})] \langle | V(K) |^2 \rangle , \tag{7}$$

where

$$\langle | V(K) |^2 \rangle = 4 \int_0^1 | V(\mathrm{K}) |^2 \, (K/2 \, k_{\mathrm{F}})^3 \, \mathrm{d}(K/2 \, k_{\mathrm{F}})$$

and

$$\begin{aligned} | V(K) |^2 &= \langle U^2 \rangle - \langle U \rangle^2 && (8) \\ &= \sum_i \sum_j c_i \, c_j \, U_i(K) \, U_j(K) \, I_{ij}(K) . \end{aligned}$$

In the above expressions Z is the effective valence and k_{F} is the Fermi radius of the alloy. The pseudopotential elements $U_i(K)$ are dimensionless and have been normalized so that

$$U_i(0) = - Z_i / Z ,$$

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[9] C. N. J. WAGNER, N. C. HALDER, and D. M. NORTH, Phys. Letters **25 A**, 663 [1967].

[12] T. E. FABER and J. M. ZIMAN, Phil. Mag. **11**, 153 [1965].

where Z_i is the valence of the element i. Furthermore the potentials are taken to be independent of alloy concentration and are derived[13] from the Animalu-Heine model pseudopotential elements $U_i^{AH}(K)$ for the pure elements[14, 15], shown in Fig. 5, i. e.,

$$U_i(K) = \frac{3\, Z_i}{2\,(E_F)_i\, Z}\, U_i^{AH}(K), \tag{9}$$

where $(E_F)_i$ is the Fermi energy of element i.

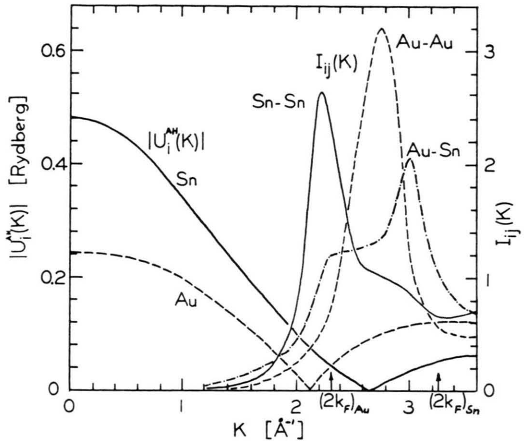

Fig. 5. Partial interference functions $I_{ij}(K)$ and pseudopotential elements $U_i(K)$ used in the calculation of the electrical resistivity ϱ_R.

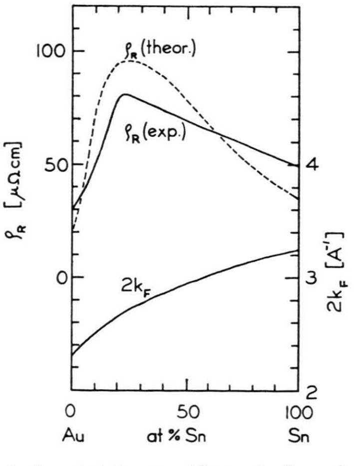

Fig. 6. Electrical resistivity ϱ_R (theoretical) and ϱ_R (experimental)[16], and Fermi diameter $2\,k_F$[17] of liquid Au-Sn alloys.

The values of ϱ_R are shown in Fig. 6 as a function of atomic concentration of Sn. Also shown are the Fermi diameters $2\,k_F$ used in the calculation of the electron transport properties, and the experimental values of ϱ_R[16, 17].

Discussion

The present analysis improves on the basic conclusion of KAPLOW, STRONG and AVERBACH[8] that the atomic distributions in liquid Au-Sn alloys are the sums of two components, i. e., Au and AuSn below 50 atomic per cent Sn concentrations and Sn and AuSn above 50 per cent Sn concentration. It indicates that a better fit of the measured $G(r)$ can be obtained when using Eq. (6) with the values of the three $G_{ij}(r)$ of Fig. 3. Such a model which describes the atomic distribution $G(r)$ as a weighted sum of three $G_{ij}(r)$ (Fig. 4) would predict a continuous variation of the thermodynamic properties as a function of concentration, in agreement with recent measurements[18]. The above results further suggest that the AuSn pair distribution in the alloys can be, at least qualitatively, described by a model based on an ordered AuSn structure.

The theoretical values of the electrical resistivity ϱ_R follow the trend of the experimental values[16, 17], i. e., Nordheim's rule is reproduced. It should be pointed out that in the calculation of ϱ_R (theoretical) of the Ag-Sn alloys[5], the pseudopotential elements for the two components were deduced from U_i^{AH}(K) in a different way, i. e.,

$$U_i^{P}(K) = (\varrho_0/\varrho_i)\; U_i^{AH}(K) \tag{10}$$

$$= \tfrac{2}{3}\, E_F[k_F/(k_F)_i]\; U_i(K), \tag{11}$$

where ϱ_i and $(k_F)_i$ are the atomic density and Fermi radius of element i, respectively, and E_F is the Fermi energy of the alloy. The term $\frac{2}{3} E_F$ appears in Eq. (11) because the value of $(2\,E_F/3)^2$ was previously[5] not factored out of $\langle |V(K)|^2 \rangle$ as done in Eq. (4) above. Using the values of $U_i(K)$ in Eq. (4) to calculate ϱ_R of Ag-Sn alloys, one finds that the theoretical values are about 20% higher than the experimental values of the resistivity.

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It must be emphasized that the agreement around the maximum in the resistivity for Au-Sn, and indeed for all noble metal-Sn alloys is purely qualitative. The resistivity integrand in Eq. (7) for high noble metal concentrations is dominated almost entirely by the low angle behaviour of the $I_{ij}(K)$ (see Fig. 5), particularly those for Au-Au and Au-Sn for example, and accurate data in this region is extremely difficult to accumulate. In addition the pseudopotential elements $U_i(K)$ for the noble metals could be questionable because of the presence of the d bands in these metals. With these limitations in mind, however, any quantitative agreement obtained between theoretical and experimental resistivity values could be fortuitous.

On Non-Ideal Conditions in Plane Source Diffusion Experiments

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The concentration in bottom layer diffusion experiments with non-ideal initial conditions is expressed as an infinite series, the first term of which represents the ideal distribution. It is shown that it is always possible to define the zero time in such a way that the approximation of the diffusion process to an ideal one is optimized.

Introduction

It is often impossible in diffusion experiments to arrange initial conditions that agree with the theoretical conditions imposed in solving the diffusion equation. Strictly speaking, the "ideal" conditions are not necessary, since the diffusion equation has a solution for any known initial distribution. For the one-dimensional case this solution is [1].

$$c = \frac{1}{2\sqrt{\pi D t}} \cdot \int_{-\infty}^{\infty} \varrho(\xi) \cdot \exp[-(x-\xi)^2/4 D t] \, d\xi \,, \quad (1)$$

where the concentration c is expressed as a function of the time t and the position coordinate x. $\varrho(x)$ is the concentration distribution at $t=0$, and the diffusion coefficent D is assumed to be constant.

The present paper is concerned with plane source diffusion (or bottom layer diffusion) only, where the system is confined to the region $x \geqq 0$, the plane $x=0$ being impermeable. In this case Eq. (1) reduces to [1]

$$c = \alpha_0 (\pi D t)^{-1/2} \cdot \exp\{-x^2/4 D t\} \,, \quad (2)$$

where α_0 is the amount of diffusing substance per unit area. It is obviously impossible to attain the initial condition strictly in this case, since $c \to \infty$ as $x \to 0$, $t=0$.

We will treat three cases:

I. A controlled addition of diffusing substance takes place at $x=0$ during a finite time interval of length Θ.

II. The arbitrary initial distribution $\varrho(x)$ at a certain moment is determined empirically.

III. The initial distribution $\varrho(x)$ cannot be determined with sufficient accuracy, but the diffusion process can be observed during a certain period of time.

I. Description with Known Rate of Solute Addition

It is often an adequate description to assume that an amount of the diffusing substance is added at $x=0$ during a finite time interval of length Θ [2]. The solution of the diffusion equation is, for $t > t_0$,

$$c = \int_{t_0-\Theta}^{t_0} m(\tau - t_0) \cdot g(x, t-\tau) \, d\tau \,. \quad (3)$$

$m(\tau - t_0)\, dt$ is the source strength during the time interval $(\tau, \tau + d\tau)$ (the term $-t_0$ in the argument of the function m is introduced for convenience in what follows), and we have used the abbreviation

$$g(x,t) \equiv (\pi D t)^{-1/2} \cdot \exp\{-x^2/4 D t\} \,. \quad (4)$$

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