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NEUTRON DIFFRACTION STUDIES OF LIQUID SILVER AND LIQUID Ag-Ge ALLOYS

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Résumé. — Une étude structurale de l'argent liquide à 1 323 K et des alliages Ag-Ge à 1 123 K a été réalisée par diffraction de neutrons. On a obtenu par transformation de Fourier les fonctions de distribution de paire $g(R)$ et calculé les nombres de coordinance. Les fonctions d'interférence expérimentales sont ensuite comparées à celles déduites d'un calcul du type Percus-Yevick. Enfin les fonctions d'interférence partielles ont été évaluées, dans l'hypothèse de leur invariance avec la concentration, pour les paires Ag-Ag et Ge-Ge. On montre qu'elles sont en très bon accord avec les facteurs de structure respectifs de l'argent et du germanium pris isolément à l'état liquide.

Abstract. — Structural studies of liquid Ag at 1 323 K and liquid Ag-Ge alloys at 1 123 K have been carried out by means of neutron diffraction. The pair correlation functions were evaluated by means of a Fourier transform and coordination numbers were calculated. The interference functions are compared with those deduced from Percus-Yevick calculation. Using the assumption of concentration independency, partial interference functions are evaluated for Ag-Ag and Ge-Ge pairs. They are shown to be very similar to the respective structure factors of liquid silver and liquid germanium.

1. Introduction. — There have been relatively few studies of liquid binary alloys by X-ray or neutron diffraction. The experimental difficulties encountered when working with such alloys (chemical reactivity at high temperature, use of isotopes, etc.) require structure studies to be carried out on a typical metallic system representing a class whose macroscopic properties have certain common characteristics.

This is the case of alloys including a metal of the type gold, silver, copper, aluminium and a semiconductor (silicon, germanium) or a semi-metal (bismuth, antimony). In fact all these systems have a phase diagram with a single eutectic the fusion temperature of which is relatively far from that of the pure elements (important eutectic effect).

On the basis of the thermodynamic properties, the

fusion heat of the eutectics has been estimated and it is found to be abnormally low (¹).

The structural study of condensed matter is most often performed by electron, X-ray or neutron diffraction. Although the last two types of radiation have many common characteristics, they differ considerably on a certain number of points [1]. The present study refers to the silver-germanium alloy. This system was chosen as an example among the metal-semiconductor alloys defined above because of its relatively favourable chemical properties for studies at high temperature. We also considered that it would be interesting to study silver under the same conditions as this had not been previously carried out by means of neutron scattering.

The crystallographic characteristics of the two

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(¹) Moquet, J. L., Private communication, 1972, LTPCM, Grenoble.

constituents silver and germanium are relatively different. Silver crystallizes in the f.c.c. system ($a_0 = 4.086 \text{ \AA}$) while germanium crystallizes in the diamond system ($a_0 = 5.657 \text{ \AA}$).

From the neutron point of view, silver and germanium have coherent scattering cross-sections of respectively 4.6 and 8.8 barns with effective absorption cross-sections of 36 and 1.3 barns for a wavelength of $1.08 \text{ \AA}$. On the other hand silver has stable isotopes (^{107}Ag and ^{109}Ag) with coherent scattering cross-sections of 8.7 ± 0.5 and 2.3 ± 0.2 barns [2] sufficiently different to permit accurate determination of the partial pair correlation functions $g_{\text{AgAg}}(R)$, $g_{\text{AgGe}}(R)$ and $g_{\text{GeGe}}(R)$ characteristic of this alloy. The experiments are currently being undertaken and will be published in the near future.

2. Basis of structural studies. — 2.1 AVERAGE COHERENT INTENSITY ⁽²⁾. — The wave amplitude diffracted by an assembly of atoms of types α ($\alpha = 0, 1, 2, \dots$) is expressed by the equation :

$$A(\mathbf{k}) = \sum_{\alpha} f_{\alpha} \sum_{i(\alpha)} \exp(-i\mathbf{k} \cdot \mathbf{r}_{i(\alpha)})$$

where $f_0, f_1, \dots$ are coherent scattering lengths of the types 0, 1, ... and $\mathbf{r}_{i(\alpha)}$ represents the position of the i th atom of species α .

The average coherent intensity is expressed as follows :

$$I_{\text{coh.}}(\mathbf{k}) = \sum_{\alpha} \sum_{\beta} f_{\alpha} f_{\beta}^* \overline{\sum_{i(\alpha)} \sum_{j(\beta)} \exp i\mathbf{k} \cdot (\mathbf{r}_{j(\beta)} - \mathbf{r}_{i(\alpha)})}.$$

If we take $\mathbf{r}_{j(\beta)} - \mathbf{r}_{i(\alpha)} = \mathbf{R}_{ji}$ this last expression becomes

$$I_{\text{coh.}}(\mathbf{k}) = \sum_{\alpha} \sum_{\beta} f_{\alpha} f_{\beta}^* \overline{\sum_{i(\alpha)} \sum_{j(\beta)} \cos \mathbf{k} \cdot \mathbf{R}_{ji}}$$

since $\overline{\sum_{i(\alpha)} \sum_{j(\beta)} i \sin \mathbf{k} \cdot \mathbf{R}_{ji}} = 0$ regardless of the values of $i(\alpha)$ and $j(\beta)$.

In the evaluation of the term $\overline{\sum_{i(\alpha)} \sum_{j(\beta)} \cos \mathbf{k} \cdot \mathbf{R}_{ji}}$, two cases must be considered :

if $i(\alpha) = j(\beta)$

$$\overline{\sum_{i(\alpha)} \sum_{j(\beta)} \cos \mathbf{k} \cdot \mathbf{R}_{ji}} = N c_{\alpha} \delta_{\alpha\beta}$$

where N is the total number of atoms, $\delta_{\alpha\beta}$ the Kronecker delta symbol and c_{α} represents the atomic concentrations such that $\sum_{\alpha} c_{\alpha} = 1$;

if $i(\alpha) \neq j(\beta)$.

By analogy with a system with a single constituent [3], a group of partial interference functions is defined in accordance with the relationships :

$$S_{\alpha\beta}(k) - 1 = \frac{1}{N c_{\alpha} c_{\beta}} \overline{\sum_{i(\alpha)} \sum_{j(\beta)} \cos \mathbf{k} \cdot \mathbf{R}_{ji}}.$$

Hence :

$$\sum_{j(\beta)} \cos \mathbf{k} \cdot \mathbf{R}_{ji} = \int \cos \mathbf{k} \cdot \mathbf{R}_{ji} d\mathcal{V}$$

with

$$d\mathcal{V} = N c_{\beta} g_{\alpha\beta}(R) \frac{d\mathbf{R}}{\Omega}$$

where Ω is the total volume of the system, $d\mathcal{V}$ the probability of finding an atom β at the centre of a small element of volume $d\mathbf{R}$ knowing that at the same time there is an atom α at the origin, $g_{\alpha\beta}(R)$ representing the pair partial correlation function.

Hence we obtain :

$$S_{\alpha\beta}(k) - 1 = \frac{1}{c_{\alpha} \Omega} \left[\overline{\int \int_{i(\alpha)} (g_{\alpha\beta}(R) - 1) \cos \mathbf{k} \cdot \mathbf{R} d\mathbf{R}} + \overline{\sum_{i(\alpha)} \int \cos \mathbf{k} \cdot \mathbf{R} d\mathbf{R}} \right].$$

The normalization conditions require that when R tends towards infinity $g_{\alpha\beta}(R)$ become equal to unity and $S_{\alpha\beta}(k)$ such that :

$$\overline{\sum_{i(\alpha)} \int \cos \mathbf{k} \cdot \mathbf{R} d\mathbf{R}} = 0.$$

If we assume that the surface particle gives a negligible contribution in the calculation of the preceding sum, we obtain (except for very small values of k) :

$$\begin{aligned} S_{\alpha\beta}(k) - 1 &= \frac{N}{\Omega} \int (g_{\alpha\beta}(R) - 1) \cos \mathbf{k} \cdot \mathbf{R} d\mathbf{R} \\ &= \frac{4\pi N}{\Omega} \int_0^{\infty} (g_{\alpha\beta}(R) - 1) \frac{\sin kR}{kR} R^2 dR. \end{aligned}$$

The average coherent intensity then becomes :

$$I_{\text{coh.}}(k) = \sum_{\alpha} \sum_{\beta} f_{\alpha} f_{\beta}^* N c_{\alpha} [\delta_{\alpha\beta} + c_{\beta} (S_{\alpha\beta}(k) - 1)].$$

2.2 BINARY SYSTEM. — For a binary system ($\alpha, \beta = 1, 2$), the average coherent intensity is expressed as follows :

$$I_{\text{coh.}}(k) = N [c_1 f_1^2 + c_2 f_2^2 + c_1^2 f_1^2 (S_{11}(k) - 1) + c_2^2 f_2^2 (S_{22}(k) - 1) + 2 c_1 c_2 f_1 f_2 (S_{12}(k) - 1)].$$

Hence the total interference function is deduced by the relationship

$$S(k) = \frac{I_{\text{coh.}}(k)}{I_{\text{coh.}}(\infty)}$$

(2) While the result of the calculations is well-known, it appears to us opportune to give the whole development which in our knowledge, cannot be found in the literature.

or

$$S(k) - 1 = \frac{c_1^2 f_1^2}{c_1 f_1^2 + c_2 f_2^2} (S_{11}(k) - 1) + \frac{c_2^2 f_2^2}{c_1 f_1^2 + c_2 f_2^2} (S_{22}(k) - 1) + \frac{2 c_1 c_2 f_1 f_2}{c_1 f_1^2 + c_2 f_2^2} (S_{12}(k) - 1) \quad (1)$$

the global interference function $S(k)$ and the partial interference functions $S_{11}(k)$, $S_{22}(k)$ and $S_{12}(k)$ relative respectively to the pairs 1, 1 ; 2, 2 and 1, 2 being normalized to unity.

The Fourier transform of the partial interference functions give pair partial correlation functions $g_{\alpha\beta}(R)$ which permit local order to be achieved.

$$g_{\alpha\beta}(R) - 1 = \frac{\Omega}{2 \pi^2 N} \int_0^\infty (S_{\alpha\beta}(k) - 1) \frac{\sin kR}{kR} k^2 dk.$$

We find that to obtain the partial interference functions $S_{\alpha\beta}(k)$, we must carry out three experiments with different $c_\alpha f_\beta$ coefficients. We can modify either the concentration c_α or the nature of the interactions represented by f_β .

The modification of concentrations is the simplest method but this implies the, rarely justified, hypothesis of the invariance of the partial interference functions with respect to the concentration. In any case, initially and to obtain a first evaluation of the partial interference functions, the hypothesis of their invariance with the concentration has been used.

In the present case of the Ag-Ge alloys, it is possible to vary the interaction intensity without changing its nature. For this it is sufficient to carry out diffraction measurements with different isotopic concentrations of silver ^{107}Ag and ^{109}Ag .

3. Experimental method. — **3.1 APPARATUS.** — The experiments were carried out as follows :

— partly on the ILL spectrometer D4 on the hot source ($\lambda = 0.697 \text{ \AA}$) [4],

— partly on the spectrometer H10 of the reactor EL3 at Saclay ($\lambda = 1.133 \text{ \AA}$) [5].

The measurements were carried out for wave-vectors $k = 4 \pi \sin \theta / \lambda$, varying from $0.10 \text{ \AA}^{-1}$ to $14.85 \text{ \AA}^{-1}$.

The samples were placed in cylindrical vanadium containers 7.6 mm in diameter and 0.2 mm thick. As regards the sample environment conditions :

1) at ILL we used a furnace consisting of a vanadium cylinder 25 mm in diameter and 0.1 mm thick,

2) at Saclay high temperature experiments were carried out with an induction heating device, the sample being by itself in the beam.

3.2 DETERMINATION OF $I_E(2\theta)$. — In order to measure the scattered intensity $I_E(2\theta)$ we used for each sample two methods of data acquisition depending on the experimental set-up.

At ILL three successive spectra were obtained ;

(i) $I_1(2\theta)$ intensity diffused by the vanadium furnace alone,

(ii) $I_2(2\theta)$ intensity diffused by the vanadium container inside the vanadium furnace ⁽³⁾,

and (iii) the $I_3(2\theta)$ intensity diffused by the sample in the vanadium container inside the vanadium furnace.

At Saclay only two spectra were obtained (because only the sample is seen by the neutron beam) [1] ;

(i) $I'_2(2\theta)$ intensity diffused only by the vanadium container,

and (ii) the $I'_3(2\theta)$ intensity diffused by the sample in the vanadium container.

The determination of this scattered intensity $I_E(2\theta)$ will be carried out in all cases taking account of the different absorption factors (see appendix 1).

It is then necessary to make a correction within the static approximation. This type of Placzek [6] correction is developed by Yarnell [7] and consists in an evaluation of this inelasticity effect. We also estimated following Blech and Averbach [8] the contribution due to multiple scattering, but this correction was not applied, as its variation of less than 1/1 000 for the whole angular range falls within the experimental statistical error.

3.3 DETERMINATION OF INTERFERENCE FUNCTIONS.

— We have determined the total interference functions for three different compositions of the Ag-Ge alloy and the structure factor of silver $S(k)$ being normalized by the following relation

$$S(k) = \frac{I_{\text{coh.}}(k)}{I_{\text{coh.}}(\infty)}.$$

If we admit that apart from coherent scattering all the other contributions (multiple scattering, incoherent scattering, etc.) are isotropic we can write :

$$I(k) = I_{\text{coh.}}(k) + X$$

where X represents the above isotropic contribution to the scattered intensity. As a result :

$$S(k) = \frac{I(k) - X}{I(\infty) - X}.$$

In particular :

$$S(0) = \frac{I(0) - X}{I(\infty) - X}.$$

⁽³⁾ In case of heating by Joule effect, using a vanadium resistor, the interest of using vanadium is that its coherent scattering cross-section is practically zero. In fact the only contribution is the completely isotropic incoherent diffusion, which simplifies the corrections.

According to thermodynamics, for a monoatomic substance :

$$S(0) = k_B T \rho_0 \beta$$

where k_B is the Boltzmann constant,
 ρ_0 is the number of atoms per volume unit,
 β is the isothermal compressibility,
 and for a binary alloy :

$$S(0) = \frac{\varphi(c_1 f_1 + c_2 f_2)^2 + A[(f_1 - f_2) - \delta(c_1 f_1 + c_2 f_2)]^2}{c_1 f_1^2 + c_2 f_2^2}.$$

In this expression

$$\varphi = k_B T \rho_0 \beta, \quad A = \frac{c_2}{\left(\frac{d \ln a_1}{dc_1}\right)_{T,P}},$$

$$\delta = \frac{1}{V_m} \left(\frac{\partial V_m}{\partial c_1} \right)_N$$

and f_1 and f_2 are the coherent scattering lengths of the constituents 1 and 2.

a_1 is the activity of the constituent 1 (Its values taken for Ag-Ge alloys are deduced from a compilation due to Hultgren [9]).

V_m is the molar volume of the alloy.

The values chosen for V_m are experimental values for pure Ag, 0.858 at % Ag and 0.759 at % Ag alloys. For the 0.402 at % Ag alloy, the value of V_m results from an extrapolation [10].

In addition the value of $I(0)$ is determined on the basis of the experimental curve which also permits one to obtain the asymptotic value of the scattered intensity $I(\infty)$ since k is sufficiently large for the interference effects not to be observable.

4. Experimental results. — **4.1 LIQUID SILVER.** — We have represented respectively in figures 1 and 2 the structure factor and the pair correlation function $g(R)$ of liquid silver at 1 323 K.

We compare, in table I below, our results with those obtained at the same temperature by Wagner *et al.* [11] and at various temperatures by Pfannenschmid [12] and Waseda *et al.* [13].

It should be noticed that there exists a general agreement with the previous results for both the $S(k)$ and the $g(R)$ features. However, in spite of the strong

FIG. 1. — Structure factor $S(k)$ of liquid silver at 1 323 K. Percus-Yevick calculation (full line). Experimental curve (open circle).

FIG. 2. — Pair correlation function $g(R)$ of silver.

absorption cross-section of silver, this first structural investigation by neutron diffraction presents a higher first peak in the $S(k)$ and a higher coordination number : 11.93 which are the main characteristics of a compact structure in the liquid state.

Moreover, in the Percus-Yevick approximation and using a hard sphere potential, we calculated the structure factor of silver with a hard sphere diameter of $R_{Ag} = 2.599$ Å evaluated according to Aschcroft *et al.* method's [14]. It will be noted that there is a very good agreement for both the positions and the intensities of all peaks values and the calculated ones as shown in figure 1.

TABLE I

References	Radiation	Temperature K	First peak position : k_1 Å ⁻¹	Second peak position : k_2 Å ⁻¹	$S(k_1)$	$S(k_2)$	R_1 Å	n_1 atoms
Pfannenschmid	X-ray	1 273	2.63	4.80	2.63	1.24	2.86	10.00
Waseda <i>et al.</i>	X-ray	1 273	2.61	4.86	2.48	1.25	2.87	11.30
Wagner <i>et al.</i>	X-ray	1 323	2.62	4.87	2.52	1.21	2.87	11.50
This work	Neutrons	1 323	2.65	4.90	2.85	1.28	2.85	11.93
Percus-Yevick approximation		1 323	2.65	4.90	2.82	1.36		

4.2 SILVER-GERMANIUM ALLOYS. — The interference functions were determined at 1 123 K. They are relative to the following alloys :

- a) Ag : 0.858 at % Ge : 0.142 at %
- b) Eutectic composition
Ag : 0.759 at % Ge : 0.241 at %
- c) Ag : 0.402 at % Ge : 0.598 at %.

Table II summarizes the characteristics of the obtained interference functions which are shown in figure 3.

FIG. 3. — Interference functions of three different Ag-Ge alloys at 1 123 K. a) $\text{Ag}_{0.858}\text{Ge}_{0.142}$, b) Eutectic $\text{Ag}_{0.759}\text{Ge}_{0.241}$, c) $\text{Ag}_{0.402}\text{Ge}_{0.598}$.

As the germanium concentration increases, we note that there is a decrease and a softening of the first maximum which corresponds to the transition from a metal type configuration to a covalent type configuration.

The pair correlation functions are shown in figure 4 and the properties of their first peak are given in table II. When the germanium concentration increases, the position of the first maximum is changing slightly to smaller values of R and the intensity of the peaks decrease for an alloy richer in germanium. Moreover, we should remark that the first minimum becomes less deep. These properties show that long-range order effects seem to disappear with increasing germanium concentration.

FIG. 4. — Pair correlation functions for : a) $\text{Ag}_{0.858}\text{Ge}_{0.142}$, b) Eutectic $\text{Ag}_{0.759}\text{Ge}_{0.241}$, c) $\text{Ag}_{0.402}\text{Ge}_{0.598}$.

The comparison with the work of Dutchak [15] is difficult as concerns the eutectic composition because he worked at a maximum temperature of 1 023 K. For all the compositions, we have calculated the interference functions in the Percus-Yevick approximation [16] (see appendix 2). The evaluated curves are shown in figure 5. The obtained hard-sphere

FIG. 5. — Interference functions obtained by means of a Percus-Yevick calculation at 1 123 K for : a) $\text{Ag}_{0.858}\text{Ge}_{0.142}$, b) Eutectic $\text{Ag}_{0.759}\text{Ge}_{0.241}$, c) $\text{Ag}_{0.402}\text{Ge}_{0.598}$.

TABLE II

Alloys		First peak position : k_1 $\text{\AA}^{-1}$		Second peak position : k_2 $\text{\AA}^{-1}$		$S(k_1)$		$S(k_2)$		R_1 $\text{\AA}$	n_1 atoms
Ag at %	Ge at %	Exp.	P.Y.	Exp.	P.Y.	Exp.	P.Y.	Exp.	P.Y.	Exp.	Exp.
0.858	0.142	2.65	2.65	5.00	4.90	2.65	2.84	1.24	1.19	2.80	11.30
0.759	0.241	2.65	2.65	5.00	4.95	2.50	2.82	1.23	1.18	2.75	10.31
eutectic											
0.402	0.598	2.62	2.65	5.05	4.95	1.71	2.81	1.17	1.16	2.70	8.58

diameters are $R_{\text{Ge}} = 2.610 \text{ \AA}$ and $R_{\text{Ag}} = 2.602 \text{ \AA}$. We find a good agreement between the position of the maxima and minima calculated and obtained by experiments for the 0.858 at % Ag alloy. This agreement is not so good for the eutectic alloy and very bad for the 0.402 at % Ag alloy. This discordance may arise from the fact that the model chosen takes into account only the size effect of the particles. In particular, it does not include the chemical interaction between the constituents. It therefore provides us with a good representation of a simple metallic system as has been shown in the case of pure silver, but it cannot take into account covalent bonding with directional effects.

On the basis of measurements of the three alloys, the partial interference functions are deduced from equation (1) using the concentration method.

The partial interference function $S_{\text{AgAg}}(k)$ is represented in the figure 6 together with the calculated $S_{\text{AgAg}}(k)$ obtained by the Percus-Yevick method for the eutectic composition. It should be noticed that a very good agreement exists between the positions and the intensities of the maxima and the minima for these two interference functions. Moreover, $S_{\text{AgAg}}(k)$ is very similar to $S(k)$ for pure silver (Fig. 1).

FIG. 6. — Partial interference function $S_{\text{Ag-Ag}}(k)$. Percus Yevick calculation deduced from an evaluation for the eutectic composition (full line). Calculated by means of concentration method using experimental results near the eutectic composition (dotted line).

FIG. 7. — Partial interference function $S_{\text{Ge-Ge}}(k)$. Experimental curve of Isherwood *et al.* at 1 277 K (full line). Calculated by means of concentration method using experimental results near the eutectic composition (open circle).

The partial interference function $S_{\text{GeGe}}(k)$, figure 7, has all the characteristics of the structure factor of pure germanium. Moreover, we obtained the resolution of the shoulder found by Hendus [17], Krebs [18], Isherwood *et al.* [19], Waseda *et al.* [20] in a second peak. The first peak is higher and sharper as shown by the curve of Mănăilă *et al.* [19] which is presented on figure 7 with $S_{\text{GeGe}}(k)$.

5. Discussion. — The determination of the structure factor of liquid silver by neutron diffraction is in very good agreement with the Percus-Yevick evaluation. This result is confirmed by the calculation of the pair correlation function and coordination number which are well representative of a compact system with pure metallic bonds. The distance R_1 of the first peak in $g(R)$ and the nearest neighbours number n_1 reported on table I lead us to assume that local order seems to be unchanged on melting.

The interference functions of the silver-germanium alloys exhibit a decreasing order as the concentration in germanium increases.

It seems that in this range of concentration around the eutectic composition the ordering effect is due to metallic bonds for silver-silver pairs very similar to those of pure silver, and bonds which recall the covalent bonding in liquid germanium at higher temperature for germanium-germanium pairs. Nothing can be concluded on the silver germanium bonding; moreover the hypothesis of unchanged partial interference functions with concentration may introduce uncertainty on their calculation. The elaboration of a complete model of local order in silver-germanium alloys needs a more accurate knowledge of all the partial interference functions and pair partial correlation functions. This studies by means of the isotopic method are now undertaken.

6. Conclusion. — The structure factor and the pair correlation function of liquid silver at 1 323 K have been determined by means of neutron diffraction. The very good agreement of the $S(k)$ with a Percus-Yevick calculation and the high value of the coordination number : 11.93 exhibit a compact local order for silver in the liquid state.

Similar experiments on the silver-germanium alloys at 1 123 K have permitted us to determine the interference functions. From these results, we have deduced the partial interference functions for silver-silver and germanium-germanium pairs which are not far from those of pure elements. In addition the present experimental results could be used to obtain the pair partial correlation functions. However, in order to achieve this result, it is necessary to check the validity of the hypothesis of invariance of partial interference functions with composition. This can be done with the aid of new experiments using alloys of variable isotopic concentration of silver. As suggested in section 1, these experiments, which are in progress, will be covered by a subsequent publication.

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Appendix 1. — By generalizing a method of calculation used by Paalman and Pings [21], the intensities : $I_1(2\theta)$, $I_2(2\theta)$ and $I_3(2\theta)$ can be expressed with the aid of the equations :

$$I_1(2\theta) = A_{F,F}(2\theta) I_F(2\theta)$$

$$I_2(2\theta) = A_{F,FC}(2\theta) I_F(2\theta) + A_{C,FC}(2\theta) I_C(2\theta)$$

$$I_3(2\theta) = A_{F,FCE}(2\theta) I_F(2\theta) + A_{C,FCE}(2\theta) I_C(2\theta) + A_{E,FCE}(2\theta) I_E(2\theta).$$

I_F is the theoretical scattering of the furnace alone,
 I_C is the theoretical scattering of the container alone,
 and

I_E is the theoretical scattering of the sample alone.

The word *theoretical scattering* indicates that the

beam has not been attenuated by either scattering or by pure absorption.

I_1 = intensity scattered by the furnace alone,

I_2 = intensity scattered by the furnace and the container, and

I_3 = intensity scattered by the furnace plus container plus sample.

$A_{F,F}$ is the absorption term due to the furnace for the scattering by the furnace ;

$A_{F,FC}$ is the absorption term due to the furnace and to the container for the scattering of the furnace ;

$A_{C,FC}$ is the absorption term due to the furnace and to the container for the scattering of the container ;

$A_{F,FCE}$ is the absorption term due to the furnace, to the container and the sample for the scattering of the furnace ;

$A_{C,FCE}$ is the absorption term due to the furnace, to the container and the sample for the scattering of the container ;

$A_{E,FCE}$ is the absorption term due to the furnace, to the container and the sample for the scattering of the sample.

They are defined by the following expressions :

$$A_{F,F}(2\theta) = \frac{1}{\pi R_F^2 (K_F^2 - 1)} \int_0^{2\pi} \int_{R_F}^{K_F R_F} \exp(-\mu_F X_F) R dR d\varphi$$

$$A_{F,FC}(2\theta) = \frac{1}{\pi R_F^2 (K_F^2 - 1)} \int_0^{2\pi} \int_{R_F}^{K_F R_F} \exp - [\mu_F X_F + \mu_C X_C] R dR d\varphi$$

$$A_{C,FC}(2\theta) = \frac{1}{\pi R_C^2 (K_C^2 - 1)} \int_0^{2\pi} \int_{R_C}^{K_C R_C} \exp - [\mu_F X_F + \mu_C X_C] R dR d\varphi$$

$$A_{F,FCE}(2\theta) = \frac{1}{\pi R_F^2 (K_F^2 - 1)} \int_0^{2\pi} \int_{R_F}^{K_F R_F} \exp - [\mu_F X_F + \mu_C X_C + \mu_E X_E] R dR d\varphi$$

$$A_{C,FCE}(2\theta) = \frac{1}{\pi R_C^2 (K_C^2 - 1)} \int_0^{2\pi} \int_{R_C}^{K_C R_C} \exp - [\mu_F X_F + \mu_C X_C + \mu_E X_E] R dR d\varphi$$

$$A_{E,FCE}(2\theta) = \frac{1}{\pi R_C^2} \int_0^{2\pi} \int_0^{R_C} \exp - [\mu_F X_F + \mu_C X_C + \mu_E X_E] R dR d\varphi$$

where $-\mu_F$, μ_C , μ_E are the absorption coefficients of the furnace, container and sample (Fig. 8).

— $K_F R_F$ and R_F are the outside and inside radius of the furnace.

— $K_C R_C$ and R_C are the outside and inside radius of the container.

If we evaluate the distance X_F covered by the neutrons in the furnace, according to figure 8

$$X_F = X_{1F} + X_{2F} = \sqrt{K_F^2 R_F^2 - X_1^2} - \sqrt{R_F^2 - X_1^2} + \sqrt{K_F^2 R_F^2 - X_2^2} - \sqrt{R_F^2 - X_2^2},$$

FIG. 8. — Evaluation of the optic path in the absorption process.

where X_1 and X_2 are smaller than R_C . It can easily be shown that as far as $R_C \ll R_F$, $\exp(-\mu_F X_F)$ is independent of R and φ such that we obtain :

$$\langle \exp(-\mu_F X_F) \rangle = \alpha'$$

thus :

$$A_{E,FCE}(2\theta) = \alpha' \int_0^{2\pi} \int_0^{R_C} \exp[-\mu_C X_C + \mu_E X_E] R dR d\varphi$$

$$A_{E,FCE}(2\theta) = \alpha' A_{E,CE}(2\theta)$$

in the same way :

$$A_{C,FCE}(2\theta) = \alpha A_{C,CE}(2\theta)$$

$$A_{C,FC}(2\theta) = \alpha A_{C,C}(2\theta)$$

The coefficients $A_{E,CE}(2\theta)$, $A_{C,CE}(2\theta)$, $A_{C,C}(2\theta)$ and $A_{F,F}(2\theta)$ are evaluated on the basis of a computer calculation. The calculation of the coefficients $A_{F,FC}(2\theta)$ and $A_{F,FCE}(2\theta)$ is more complicated and has necessi-

tated a special program. The intensity $I_E(2\theta)$ scattered by the sample thus appears in the following form :

$$I_E(2\theta) = \frac{1}{\alpha' A_{E,CE}(2\theta)} \left[I_3(2\theta) - \frac{A_{C,CE}(2\theta)}{A_{C,C}(2\theta)} I_2(2\theta) + \left(\frac{A_{C,CE}(2\theta)}{A_{C,C}(2\theta)} \frac{A_{F,FC}(2\theta)}{A_{F,F}(2\theta)} - \frac{A_{F,FCE}(2\theta)}{A_{F,F}(2\theta)} \right) I_1(2\theta) \right]$$

Appendix 2. — For a two-component system, the P.Y. equation may be written :

$$C_{\alpha\beta}(R) = g_{\alpha\beta}(R) \left[1 - \exp \frac{U_{\alpha\beta}(R)}{k_B T} \right]$$

where the $C_{\alpha\beta}(R)$ are the direct correlation functions and $U_{\alpha\beta}(R)$ are the pair potentials.

The solutions for the special case of hard-sphere interactions between the components have been given in detail by Lebowitz [16] and discussed by Ashcroft *et al.* [22]. We repeat these briefly in the following :

$$\begin{aligned} - C_{11}(R) &= a_1 + b_1 R + dR^3 & R < \sigma_1 \\ - C_{22}(R) &= a_2 + b_2 R + dR^3 & R < \sigma_2 \\ - C_{12}(R) &= a_1 & R < \frac{1}{2}(\sigma_2 - \sigma_1) \\ &= a_1 + [br^2 + 4dr^3 + dr^4]/R & \frac{1}{2}(\sigma_2 - \sigma_1) < R < \frac{1}{2}(\sigma_2 + \sigma_1) \end{aligned}$$

where $r = R - \frac{1}{2}(\sigma_2 - \sigma_1)$.

The a_1, b_1, d, a_2, b_2 coefficients depend only on the diameters σ_1 and σ_2 of the hard spheres, the density ρ_1 and ρ_2 and the total packing fraction for the mixture η . We recall the definition of η :

$$\begin{aligned} \eta &= \frac{\text{volume occupied by hard spheres}}{\text{volume total}} \\ &= \frac{\pi}{6} [\rho_1 \sigma_1^3 + \rho_2 \sigma_2^3] \end{aligned}$$

The $C_{\alpha\beta}(k)$ functions are evaluated by Fourier transform of the $C_{\alpha\beta}(R)$. Then by means of the Ornstein-Zernike relations, the $S_{\alpha\beta}(k)$ functions are deduced.

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