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Temperature Dependence of the Total Interference Functions of Liquid Cu-Sn Alloys*

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The total interference function $I(K)$, which is a weighted sum of the partial interference functions, and the corresponding weighted distribution function have been calculated from the elastic x-ray scattering of liquid Cu-Sn alloys with 20 and 22.5 at.% Sn measured at temperatures between 800 and 1160°C. The total $I(K)$ of the alloys show a slight decrease in the position $K_1 = 4\pi(\sin\theta_1)/\lambda$ and in height of the first peak with increasing temperature [$K_1 = 2.88$ Å^{-1} and $I(K_1) = 3.05$ at 800°C, and $K_1 = 2.86$ Å^{-1} and $I(K_1) = 2.50$ at 1160°C]. On using the total $I(K)$ in the Faber-Ziman theory of electrical resistivity ρ_R and thermoelectric power Q of binary liquid alloys, one obtains theoretical values of ρ_R and Q which decrease slightly with increasing temperature in agreement with the experimental results of Roll and Motz and Howe, respectively.

INTRODUCTION

The temperature dependence of the interference function $I(K)$, where $K = 4\pi(\sin\theta)/\lambda$, of liquid metals and alloys can be investigated by elastic scattering experiments where x rays and neutrons are the most common radiation probes used. Structural information such as the interatomic separation r_1, and the number of atoms in the first coordination shell η, can be obtained on Fourier transformation of the data into r space. This information does not vary much as a function of increasing temperature, and, as a consequence, experimental measurements must be precise in order to determine these changes accurately.

On the other hand, the theory of electron transport properties as formulated by Ziman,[1] Bradley *et al.*,[2] and Faber and Ziman[3] utilizes directly the experimentally accessible quantity, namely $I(K)$. Significant changes in the magnitude of the first peak with temperature do occur in $I(K)$ and, most certainly for polyvalent metals, the transport properties should be more sensitive to temperature changes than the values of r_1 and η obtained from the atomic distribution function $\rho(r)$. Most liquid metals possess a positive temperature coefficient of resistivity, and use of Ziman's theory for trivalent thallium[4] and tetravalent lead[5] and tin[6] led to good quantitative agreement with the experimental coefficients. However, poor agreement was achieved for trivalent indium[7] and for monovalent sodium.[8] From the latter result it was concluded that the Born approximation, fundamental to the Ziman formalism, breaks down. This conclusion, however, has recently been challenged.[9] No study has yet been made on the divalent liquids zinc and cadmium, which possess negative temperature coefficients of resistivity, and which could offer a further test of the Ziman transport theory.

There is another class of examples of liquids where the electrical resistivity decreases or does not change with increase in temperature,[10,11] e.g., liquid Cu-Sn and Ag-Sn alloys of compositions of about 20–25 at.% Sn. Alloys with these Sn concentrations possess a Fermi diameter $2k_F$ which falls very close to the position of the first maximum K_1 of the interference function $I(K)$. In other words the theoretical arguments which are applicable to liquid divalent metals might be useful to explain the behavior of the above alloys in the liquid state.[2,11]

In this paper we present an x-ray investigation of the temperature dependence of the structure of liquid Cu-Sn alloys with 20 and 22.5 at.% Sn and report some results on the temperature dependence of the electronic transport properties. The structure of liquid binary alloys is characterized by three partial interference functions[3,12–14] $I_{ij}(K)$ which describe the pair distributions $\rho_{ij}(r)$ in K space. As pointed out by Enderby *et al.*[15] the determination of the $I_{ij}(K)$ in a liquid binary alloy is a difficult experimental problem, and it may be clearly anticipated that a study of the temperature dependence of $I_{ij}(K)$ is far more tedious. Consequently, we have chosen the total interference function which is the weighted sum of the three $I_{ij}(K)$ for the evaluation of the electrical resistivity ρ_R and the thermoelectric power Q. This approximation should be expected to yield reasonable results, since the total $I(K)$ of Cu-Sn alloys with 20 and 22.5 at.% Sn are heavily weighted by $I_{\mathrm{CuCu}}(K)$ and $I_{\mathrm{CuSn}}(K)$ whose positions K_1 of the first maximum occur roughly at the same K values as shown by Enderby *et al.*[15]

EXPERIMENTAL PROCEDURE AND RESULTS

The procedure for the alloy preparation was similar to that described by Joshi and Wagner.[16] The alloy specimens consisted of 20 and 22.5 at.% Sn of 99.99% purity and the remainder Cu of 99.99% purity. The experimental arrangement and details of data processing can be found elsewhere.[4,16] Mo $K\alpha$ radiation reflected from a quartz crystal was used. The measurements were made between $K_{\min} = 1.4$ to $K_{\max} = 15.6$ Å^{-1}, where $K = 4\pi(\sin\theta)/\lambda$. The data were recorded at temperatures between 800 and 1160°C.

The total interference function $I(K)$ can be calculated from the elastically scattered x-ray intensity per atom expressed in electron units, i. e., $I_a(K)$:

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

where $\langle f\rangle$ and $\langle f^2\rangle$ are the mean and mean square average of the atomic scattering factor of the alloy. $I(K)$ is the weighted sum of the partial interference functions $I_{ij}(K)$, i. e.,[3,12]

$$I(K) = \sum_i \sum_j \frac{c_i c_j f_i f_j I_{ij}(K)}{\langle f\rangle^2} , \qquad (1)$$

where c_i is the atomic concentration of element i. $I_{ij}(K)$ is related to the Fourier transform of the atomic density $\rho_{ij}(r)$ which represents the number of j-type atoms per unit volume at the distance r from an i-type atom. For large r, $\rho_{ij}(r)$ tends towards $\rho_j = c_j \rho_0$, where ρ_0 is the average atomic density of the alloy. $I_{ij}(K)$ can be written as

$$I_{ij}(K) = 1 + \int 4\pi r^2 \left[\frac{\rho_{ij}(r)}{c_j} - \rho_0\right] \frac{\sin Kr}{Kr} \, dr . \qquad (2)$$

The Fourier transform of $K[I(K)-1]$ yields the weighted reduced distribution function $G(r)$, i. e.,

$$G(r) = 4\pi r[\rho(r) - \rho_0] = (2/\pi)\int K[I(K) - 1] \sin Krd K ,$$

where

$$\rho(r) = \sum_i \sum_j \frac{c_i c_j f_i f_j \rho_{ij}(r)}{c_j \langle f\rangle^2} ,$$

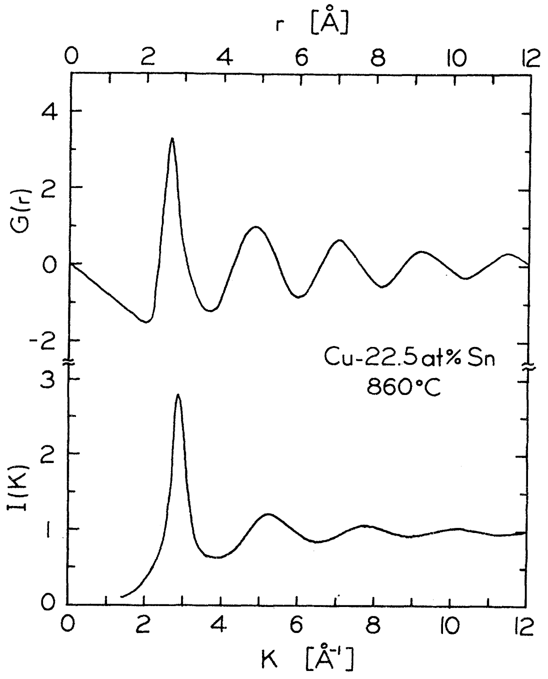

FIG. 1. Interference function I(K) and reduced distribution function $G(r) = 4\pi r[\rho(r) - \rho_0]$ for liquid Cu – 22.5 Sn measured at 860° C.

assuming that $f_i/\langle f\rangle$ is independent of K.

The total interference functions $I(K)$ and the weighted reduced distribution functions $G(r)$ are shown in Fig. 1 for Cu–22.5 at.% Sn measured at 860°C. The values of $I(K)$ between K=1.4 and 4.0 Å^{-1} are shown in Figs. 2 and 3 for the alloys measured at different temperatures.

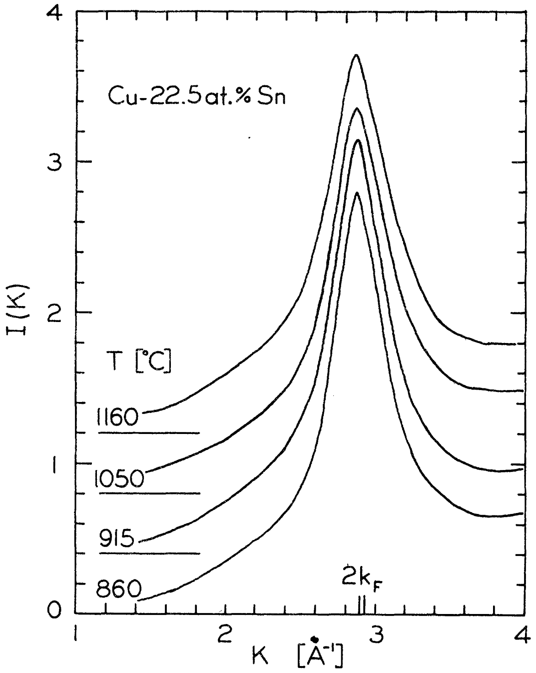

FIG. 2. Interference function I(K) of Cu – 22.5 at.% Sn measured at different temperatures T.

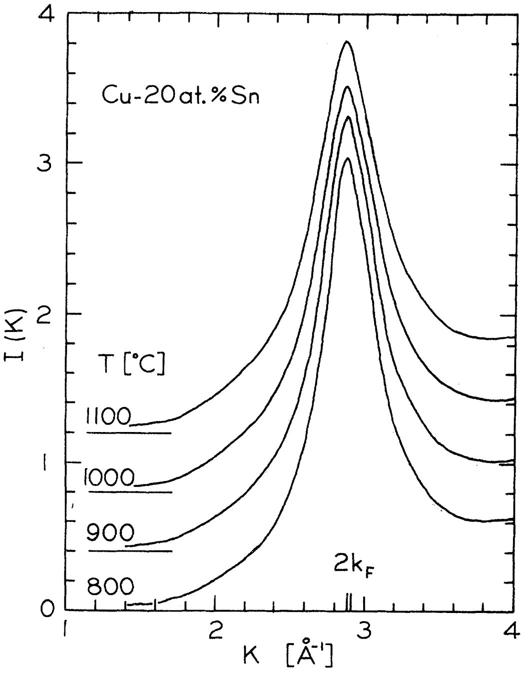

FIG. 3. Interference function I(K) of Cu – 20 at.% Sn measured at different temperatures T.

DISCUSSION

Interference Functions

The total interference functions $I(K)$ change very little within the temperature range of investigation (see Figs. 2 and 3) except for the peak heights of the first maximum which change from 3.05 at 800°C to 2.5 at 1160°C. The positions K_1 of the first peak maxima vary from 2.88 Å^{-1} at 800°C to 2.86 Å^{-1} at 1160°C which is within the experimental error of measurements, usually ± 0.02 Å^{-1}.

For the Cu-20 at.% Sn alloy, we can write

$$I(K) \simeq 0.5 I_{\mathrm{CuCu}}(K) + 0.4 I_{\mathrm{CuSn}}(K) + 0.1 I_{\mathrm{SnSn}}(K) , \qquad (3)$$

i.e., $I(K)$ is heavily weighted by the CuCu and CuSn partial interference functions. Since $I(K)$ does not change its position K_1 of the first peak maximum significantly and does not broaden drastically, it is concluded that the positions K_1 of $I_{ij}(K)$ do not vary with temperature either.

Some data for liquid Cu_3Sn have recently been published by Enderby *et al.*,[17] and it would seem reasonable to make a qualitative comparison of the present results for 22.5% Sn with those of liquid Cu_3Sn. Figure 4 shows the plots of the elastically scattered intensity $I_a[(\sin\theta)/\lambda]$. The results for Cu-22.5 at.% Sn measured at 860°C agree well with the x-ray result of Williams and Orton,[18] taken at 768°C. Poorer agreement is obtained with the scattering pattern for x rays which was calculated by Enderby *et al.*[17] from the partial interference functions $I_{ij}(K)$ measured in a Cu-45 at.% Sn alloy using neutron techniques and assuming that the $I_{ij}(K)$ are independent of the relative abundance of the elements in the alloy. In addition, the percentage error involved in $I_{ij}(K)$ is about 10%. It is, therefore, not surprising that both the x-ray results which agree rather well amongst themselves are in slight disagreement with this calculated curve.

Distribution Functions of the Alloys

The reduced distributions

$$G(r) = 4\pi r[\rho(r) - \rho_0]$$

of the alloys (see Fig. 1) resemble those of pure liquid metals. The interatomic distances r_1 obtained from the peak maximum positions of the first peak in the radial distribution function $4\pi r^2\rho(r)$ have the same value 2.7 Å at all measured temperatures. The coordination number η decreases from 12 at 800°C to 10.5 at 1160°C. In the region of small r, i.e., below $r = 2$ Å, the $G(r)$ functions were refined after Kaplow *et al.*[19]

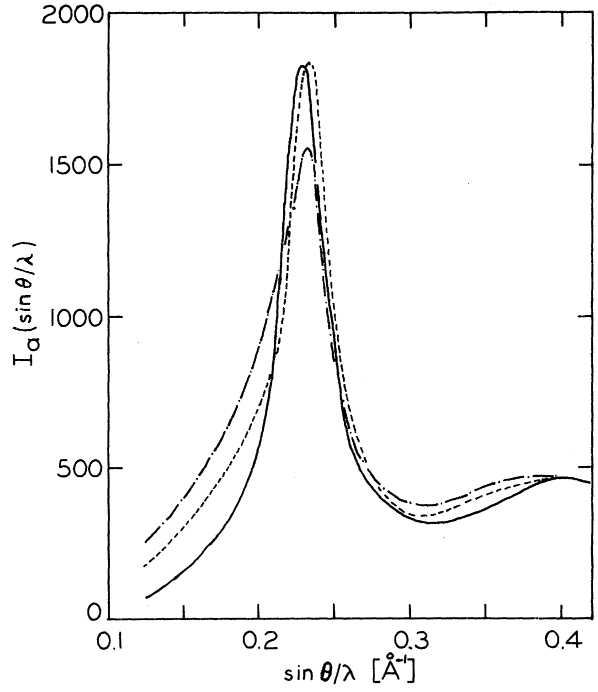

FIG. 4. Comparison of the elastically scattered intensity $I_a[(\sin\theta)/\lambda]$ per atom from the Cu-Sn alloys near the melting points. The solid curve denotes the present curve for Cu–22.5 Sn at 860°C. The dashed curve denotes the x-ray measurement of Williams and Orton[17] for Cu_3Sn. The dashed-dotted curve denotes the calculated x-ray scattering pattern of Enderby *et al.*[16] for Cu_3Sn.

Electronic Transport Properties

The application of the Faber-Ziman theory[3] for the calculation of the electrical resistivity in liquid binary alloys requires a knowledge of the matrix elements of the pseudopotentials of the ions $U_i(K)$ and the three partial interference functions $I_{ij}(K)$ of the alloy. The resistivity ρ_R is given by the relation[14]

$$\rho_R = [(\pi^3\hbar Z)/(e^2 k_F)]\langle | V(K)|^2\rangle , \qquad (4)$$

where $\langle | V(K)|^2\rangle = 4\int_0^1 | V(K)|^2 \left(\frac{K}{2k_F}\right)^3 d\left(\frac{K}{2k_F}\right)$

and

$$| V(K)|^2 = \langle U^2\rangle - \langle U\rangle^2 + \sum_i \sum_j c_i c_j U_i(K) U_j(K) I_{ij}(K) .$$

With the assumption that the pseudopotentials are local and dependent only on the magnitude of K, the well-known expression for the thermoelectric power results:

$$Q = -\frac{\pi^2 k_B{}^2 T}{3|e|E_F}\left(3 - 2\frac{| V(2k_F)|^2}{\langle | V(K)|^2\rangle}\right) . \qquad (5)$$

In the above expressions Z is the effective valence of the alloy, k_B is the Boltzmann constant, and k_F and E_F are the Fermi radius and energy, respectively, of the alloy. The $U_i(K)$ used in the expressions above are dimensionless and have been normalized so that $U_i(0) = -Z_i/Z$. Furthermore the potentials are taken to be independent of alloy concentration and are derived from the Animalu-Heine model pseudopotentials $U_i^{\mathrm{AH}}(K)$ for the pure elements as follows:

$$U_i(K) = U_i^{\mathrm{AH}}(K)(Z_i/Z)/\tfrac{2}{3}(E_F)_i \,. \tag{6}$$

Here $(E_F)_i$ is the Fermi energy and Z_i is the valence of element i. Previously[12] the values $U_i^P(K)$ defined as

$$U_i^{P}(K) = U_i^{\mathrm{AH}}(K)\frac{\rho_0}{\rho_i} = \frac{2}{3}E_F \frac{k_F}{(k_F)_i} U_i(K) \tag{7}$$

have been used in the calculation of ρ_R. The term $\frac{2}{3}E_F$ appears in Eq. (7) because the value of $[\frac{2}{3}E_F]^2$ was previously[12] not factored out of $\langle |V(K)|^2\rangle$ as done in Eq. (4) above. Assuming that $U_i(K)$ [Eq. (5)] is insensitive to changes in temperature, the values of $U_i(K)$ chosen will affect the absolute magnitude of the predicted resistivity ρ_R, but not its over-all temperature dependence.

In the evaluation of ρ_R [Eq. (3)] and Q [Eq. (4)], one should know the partial interference functions $I_{ij}(K)$ in addition to the pseudopotential elements $U_i(K)$. If the atoms in the alloy are randomly distributed, i.e.,

$$I_{11}(K) = I_{22}(K) = I_{12}(K) = I(K),$$

the measured $I(K)$ may be used; i.e., the substitutional model as proposed by Faber and Ziman[3] might be applicable. It has been demonstrated earlier[12,13] that one can employ this model with reasonable success to a large number of liquid binary alloy systems where the three partial interference functions are not known. This procedure yielded encouraging results for liquid Hg-Tl and Ag-Sn alloys.[12] Small differences in the actual values of the predicted resistivity were found when using the total and the three partial interference function in the case of Ag-Sn alloys.[13] But the overall variation of ρ_R as a function of concentration was in very good agreement with the experimental results of Roll and Motz.[10] Ashcroft and Langreth[14] have reached a similar conclusion when using their theoretically computed interference functions from the Percus-Yevick equation, together with their model pseudopotentials.

As mentioned earlier, a study of the temperature dependence of $I_{ij}(K)$ is extremely difficult. Consequently, we have chosen the total interference function $I(K)$, which is a weighted sum of the three $I_{ij}(K)$, for the evaluation of the electrical resistivity ρ_R [Eq. (4)] and the thermoelectric power Q [Eq. (5)]. The total $I(K)$ of Cu-Sn alloys with 20 and 22.5 at.% Sn are heavily weighted by $I_{\mathrm{CuCu}}(K)$ and $I_{\mathrm{CuSn}}(K)$ [Eq. (3)], whose positions K_1 of the first maximum occur roughly at the same K values as shown by Enderby *et al.*[15] Therefore it is assumed that the temperature dependence of $I_{ij}(K)$ is faithfully reproduced in $I(K)$. The pseudopotential elements of Animalu[20] for Cu and Animalu and Heine[21] for Sn have been used in the calculation of ρ_R and Q, which are plotted in Fig. 5 as a function of temperature T. Also shown are the macroscopic densities ρ, determined from the data of Bornemann and Sauerwald,[22] and the Fermi diameters $2k_F$ used in the calculation of the electron transport properties. Both ρ_R and Q show a negative temperature coefficient in agreement with the experimental data for ρ_R of Roll and Motz[10] and for Q of Howe.[23] The difference in magnitude between predicted and experimental values is probably due to the uncertainties in the pseudopotential elements $U_i(K)$ of Cu and Sn in the alloys. Another possible source for the discrepancy might be the use of the total interference function rather than the partial functions $I_{ij}(K)$. If we were to assume that $I_{ij}(K)$ are independent of concentration as suggested by Enderby *et al.*[16] and Halder and Wagner[13] we can use the experimentally determined[15] $I_{ij}(K)$ to calculate ρ_R at the liquidus temperature. A value of $\rho_R = 83$ μΩ cm is then obtained which is slightly larger than the experimental value of 74 μΩ cm. Ashcroft and Langreth[14] calculated a value of 63 μΩ cm for the electrical resistivity using their theoretical interference functions for Cu-20 at.% Sn alloy.

The thermoelectric power Q is very sensitive to the value of $U_i(2k_F)$. It is, therefore, not sur-

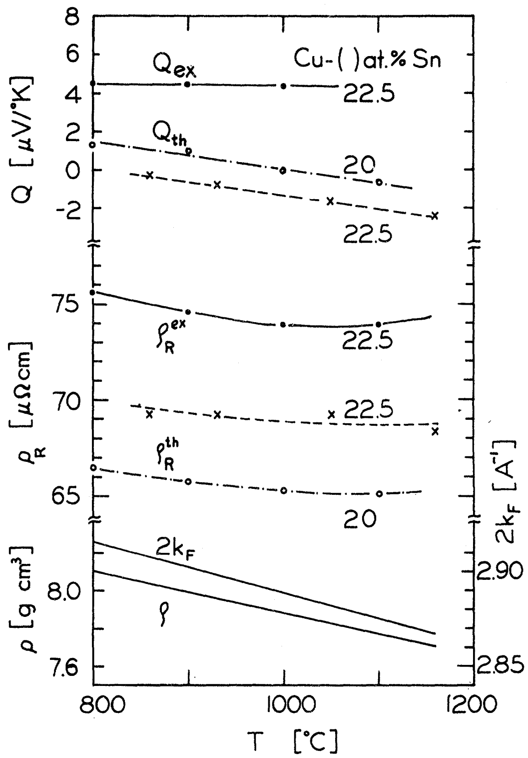

FIG. 5. Electrical resistivity ρ_R and thermoelectric power Q for liquid Cu-Sn alloys with 20 and 22.5 at.% Sn. The closed circles are the experimental points of Roll and Motz[9] and Howe,[22] and the open circles and crosses are the predicted points from the present analysis. Values of the macroscopic density ρ [21] and the Fermi diameter $2k_F$ are also given.

prising that the discrepancy in sign of Q appears. If we were to choose $U_i^P(K)$ as given in Eq. (7), values between $Q = 2.8$ μV/°K at 860°C and 1.8 μV/°K at 1160°C are calculated for the Cu–22.5 at.% Sn alloy which are in better agreement with Howe's data[23] of 4.5 μV/°K.

CONCLUSIONS

The temperature dependence of the total interference function $I(K)$ has been measured between temperatures $T = 800$ and 1160°C for Cu-Sn alloys with 20 and 22.5 at.% Sn. These alloys show a negative temperature coefficient of the electrical resistivity ρ_R. As shown by Busch and Güntherodt,[11] alloys whose interference functions have a first peak maximum at K values close to the Fermi diameter $2k_F$ possess a negative $d\rho_R/dT$. Applying the Faber-Ziman theory[3] and assuming that the temperature dependence of the partial interference functions which describe the atomic arrangement in the alloys is faithfully reproduced in the total interference function, values of the electrical resistivity and thermoelectric power have been calculated which are in good agreement with the experimental values of Roll and Motz[10] and Howe,[23] respectively.

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[1] J. M. Ziman, Phil. Mag. 6, 1013 (1961).

[2] C. C. Bradley, T. E. Faber, E. G. Wilson, and J. M. Ziman, Phil. Mag. 7, 865 (1962).

[3] T. E. Faber and J. M. Ziman, Phil. Mag. 11, 153 (1965).

[4] N. C. Halder and C. N. J. Wagner, J. Chem. Phys. 45, 482 (1966).

[5] D. M. North, J. E. Enderby, and P. A. Egelstaff, J. Physics. 1, 1075 (1968).

[6] D. M. North and C. N. J. Wagner, unpublished.

[7] H. Ocken and C. N. J. Wagner, Phys. Rev. 149, 122 (1966).

[8] A. J. Greenfield, Phys. Rev. Letters 16, 6 (1966).

[9] P. D. Adams and N. W. Ashcroft, Advan. Phys. 16, 597 (1967).

[10] A. Roll and H. Motz, Z. Metallk. 48, 435 (1957).

[11] G. Busch and H. J. Güntherodt, Physik Kondensierten Materie 6, 325 (1967).

[12] C. N. J. Wagner and N. C. Halder, Advan. Phys. 16, 241 (1967).

[13] N. C. Halder and C. N. J. Wagner, J. Chem. Phys. 47, 4385 (1967).

[14] N. W. Ashcroft and D. C. Langreth, Phys. Rev. 159, 500 (1967); and Erratum, Phys. Rev. 166, 934 (1968).

[15] J. E. Enderby, D. M. North, and P. A. Egelstaff, Phil. Mag. 14, 961 (1966).

[16] M. L. Joshi and C. N. J. Wagner, Z. Naturforsch. 20a, 564 (1865).

[17] J. E. Enderby, D. M. North, and P. A. Egelstaff, Advan. Phys. 16, 171 (1967).

[18] G. I. Williams and B. R. Orton (quoted from Ref. 17).

[19] R. Kaplow, S. L. Strong, and B. L. Averbach, Phys. Rev. 138, A1336 (1965).

[20] A. O. E. Animalu, private communication.

[21] A. O. E. Animalu and V. Heine, Phil. Mag. 12, 1249 (1965).

[22] K. Bornemann and F. Sauerwald, Z. Metallk. 14, 145 (1922).

[23] R. A. Howe, Ph. D. thesis, University of Sheffield, 1967 (unpublished).