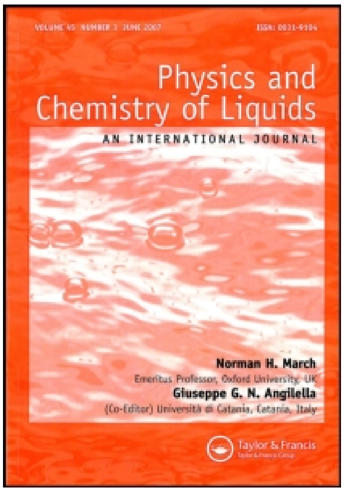

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Partial Interference and Pair Correlation Functions, Thermoelectric Power, and Electrical Resistivity of Molten Cu–Sb Alloys

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Abstract—Using the assumption of concentration independency, partial functions are calculated from experimental interference functions of molten Cu–Sb alloys reported earlier. The partial radial distribution functions yield partial coordination numbers from which by a weighted sum the total coordination numbers can be calculated. The comparison of these calculated values with the coordination numbers obtained directly from the total RDF shows good agreement. The partial coordination numbers confirm the compound formation in the melts of certain composition, whereas the tendency for segregation existent in the concentration range from 61 to 90 a/o Sb is not indicated by these numbers. The distances r_I given by the partial RDF can be composed by a weighted sum which shows good agreement with the experimental values.

As an application of the partial functions, the electrical resistivity and the thermoelectrical power were calculated. The calculated electrical resistivity shows good agreement with measured values. The calculated thermoelectrical power deviates from the experimental values for copper. The agreement for antimony is quite good. For the alloys no experimental values exist. It can be stated, that the partial functions deduced by the assumption of concentration independency are suitable functions for the interpretation of structural and electrical behaviour of molten alloys in the system Cu–Sb.

1. Introduction

In Ref. 1 the results of neutron and X-ray scattering experiments with molten alloys of the system Cu–Sb were reported. During the present work, partial interference and pair correlation functions shall be calculated from the total functions.

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2. Theoretical Outline

The total interference functions of binary alloys, obtained with X-rays can be split up according to the well known Eq. (1) into three partial interference functions I_{11}, I_{22} and I_{12}:

$$I(s) = w_{11}I_{11}(s) + w_{22}I_{22}(s) + 2w_{12}I_{12}(s) \tag{1}$$

with the weighting factors, thought to be independent of s:

$$w_{ij} = \sum_i \sum_j c_i c_j f_i(s) f_j(s) / \langle f(s) \rangle^2 \tag{2}$$

and

$$\begin{aligned} I_{11}(s) &= 1 + \int_0^\infty 4\pi r^2 \left[\frac{\rho_{11}(r)}{c_1} - \rho_0\right] \frac{\sin sr}{sr}\,\mathrm{d}r \\ I_{22}(s) &= 1 + \int_0^\infty 4\pi r^2 \left[\frac{\rho_{22}(r)}{c_2} - \rho_0\right] \frac{\sin sr}{sr}\,\mathrm{d}r \\ I_{12}(s) &= 1 + \int_0^\infty 4\pi r^2 \left[\frac{\rho_{12}(r)}{c_2} - \rho_0\right] \frac{\sin sr}{sr}\,\mathrm{d}r \end{aligned} \tag{3}$$

The ρ_{ij} mean the partial atomic densities, which describe the distribution of the 1 atoms around a 1 atom, of the 2 atoms around a 2 atom etc. Furthermore the relationship

$$c_i\,\rho_{ij} = c_j\,\rho_{ji} \tag{4}$$

is valid.

Equations (1) and (2) also hold for neutron diffraction if the atomic scattering factors for X-rays $f(s)$ are replaced by the nuclear coherent scattering amplitudes b. For the determination of the three partial interference functions I_{ij}, three independent Eqs. (1), i.e. three scattering experiments are needed, for example, one X-ray diffraction experiment and two neutron diffraction experiments using different isotopes. Up to date only one experiment of this kind was reported.(2) In all the other cases, where partial interference functions were determined (Ag–Mg,(3) Al–Au,(4) Mg–Sn,(5) Au–Sn,(6) Ag–Sn,(7) Cu–Ge,(8) and Cu–Sn(9)) concentration independency of the partial functions was assumed. According to this fact only three diffraction experiments with different concentrations are needed for the determination of the partial interference functions. This method was also used in the present work. Three total X-ray interference functions were used for the calculation of the partial interference functions. Then these functions were refined by a least squares method using three neutron interference functions at the corresponding concentrations.

From the partial interference functions partial pair correlation functions can be calculated by Fourier transformation:

$$G_{11}(r) = 4\pi r\left(\frac{\rho_{11}(r)}{c_1} - \rho_0\right) = \frac{2}{\pi}\int_0^\infty s(I_{11}(s) - 1)\sin sr\,ds$$

$$G_{22}(r) = 4\pi r\left(\frac{\rho_{22}(r)}{c_2} - \rho_0\right) = \frac{2}{\pi}\int_0^\infty s(I_{22}(s) - 1)\sin sr\,ds$$

$$G_{12}(r) = 4\pi r\left(\frac{\rho_{12}(r)}{c_2} - \rho_0\right) = \frac{2}{\pi}\int_0^\infty s(I_{12}(s) - 1)\sin sr\,ds \qquad (5)$$

According to Eq. (5) the partial pair correlation functions contain the concentration and the mean atomic density ρ_0.

Stating concentration indepency for the partial interference functions, this also must be valid for the partial pair correlation functions. Therefore the following equation is valid:

$$\frac{\rho_{ij}}{c_j} - \rho_0 = \kappa \qquad (6)$$

κ = constant, independent of concentration.

From the partial pair correlation functions $G_{ij}(r)$, the total pair correlation functions can be composed according to:

$$G(r) = \sum w_{ij}^x G_{ij}(r) \qquad (7a)$$

$$G(r) = \sum w_{ij}^N G_{ij}(r) \qquad (7b)$$

w_{ij}^x and w_{ij}^N are the weighting factors given by Eq. (2), if the $f(s)$ are replaced by the atomic numbers Z for X-rays and by the nuclear coherent scattering amplitudes b for neutrons. Thus for the same alloy concentration, two $G(r)$ are calculated which can directly be compared with the corresponding total $G(r)$, obtained by Fourier transformation of $s(I(s) - 1)$ from the X-ray and neutron data.

Agreement, once between the total pair correlation function obtained from X-ray data, denoted as $G^x(r)$, and the weighted sum $\sum w_{ij}^x G_{ij}(r)$, and on the other hand between $G^N(r)$, obtained from neutron data, and $\sum w_{ij}^N G_{ij}(r)$, will give evidence that the partial pair correlation functions are representative of the atomic arrangement in the examined liquid binary alloy.

From the partial atomic densities the partial RDF are obtained by multiplication with $4\pi r^2$. From the partial RDF the coordination number and the radius of the first coordination sphere surrounding an arbitrary atom can be deduced. The partial coordination numbers are given by

$$z_{ij} = \int_{r_1}^{r_2} 4\pi r^2 \rho_{ij}(r)\,\mathrm{d}r \tag{8}$$

In this formula, the values r_1 and r_2 determine the area beyond the first maximum of the partial RDF as the region of integration. The weighted sum of these values yields the total coordination number z:

$$z = \frac{c_1 f_1^2(s)}{\langle f(s)\rangle^2} z_{11} + \frac{c_2 f_2^2(s)}{\langle f(s)\rangle^2} z_{22} + \frac{2c_1 f_1(s) f_2(s)}{\langle f(s)\rangle^2} z_{12} \tag{9}$$

The agreement of the experimental values z and the values for z calculated according to Eq. (9) shows the reliability of the assumptions, which were applied during the calculation of the partial functions.

3. Results

The partial interference functions were determined from total interference functions⁽¹⁾ of Cu–Sb alloys with 20.5 up to 52 at.-% Sb. Other calculations with interference functions of alloys with other concentrations, show that the partial interference functions given in Fig. 1 are valid for the whole region of concentration.

The functions $I_{\mathrm{Cu-Cu}}$ and $I_{\mathrm{Sb-Sb}}$ show similarity with the interference functions of the molten pure metals. The function $I_{\mathrm{Cu-Sb}}$ shows its first maximum at $s = 2.95\,\text{Å}^{-1}$. This is the same value as with the total interference functions for alloys with 25 up to 40 at.-% Sb.

Figure 2 shows the partial pair correlation functions calculated according to Eq. (5) from the partial interference functions of Fig. 1. As to be expected from the partial interference functions, the pair correlation functions $G_{\mathrm{Cu-Cu}}$ and $G_{\mathrm{Sb-Sb}}$ show their first maximum at the same value r_I, as the total pair correlation function of the pure components. The function $G_{\mathrm{Cu-Sb}}$ shows its first maximum at $r_I = 2.63\,\text{Å}$.

From these functions, which also are independent from the concentration, the partial RDF $4\pi r^2\rho_{ij}(r)$ are obtained, which yield the number of j-atoms within a spherical shell of thickness dr in the distance r of an i-atom. Thus it can be determined the number of atoms of a certain kind around certain reference atoms. The number of atoms of one kind, which are present within the first coordination sphere, is called partial coordination number. From these numbers according to Eq. (9) the total coordination number $\sum z_{ij}$ can be composed. This calculated number is shown in Fig. 3 together with the experimentally⁽¹⁾ obtained total coordination number z_{exp} and the partial coordination numbers. It is obvious that the values $\sum z_{ij}$ are smaller than the values z_{exp}, but the deviation amounts to less than 10%. This accordance shows the good validity of the partial interference functions. The segregation tendency at higher Sb-concentrations reported in an earlier work,⁽¹⁾ cannot be derived from the partial coordination numbers. The tendency for compound formation at lower Sb-concentrations, however, can be stated.

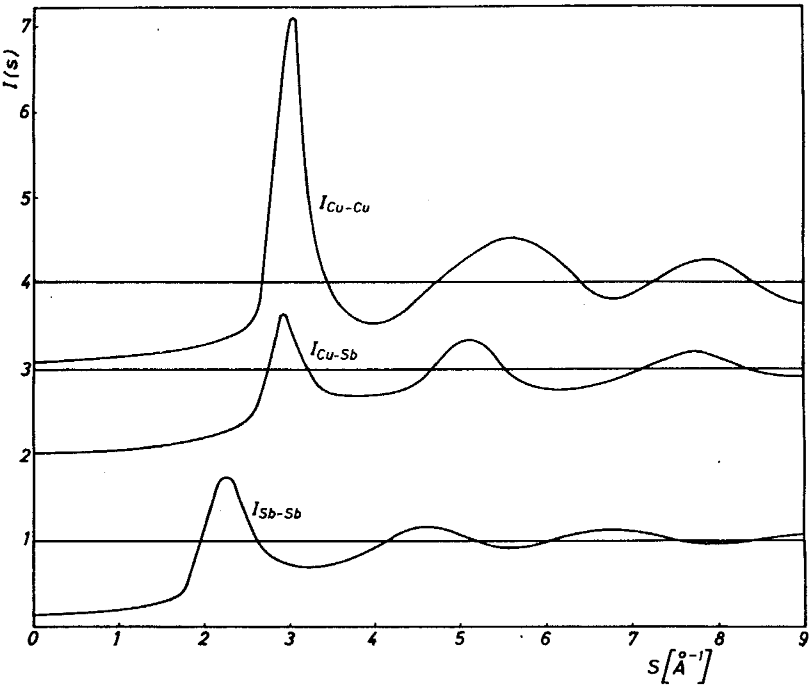

Figure 1. Partial interference functions $I(s)$.

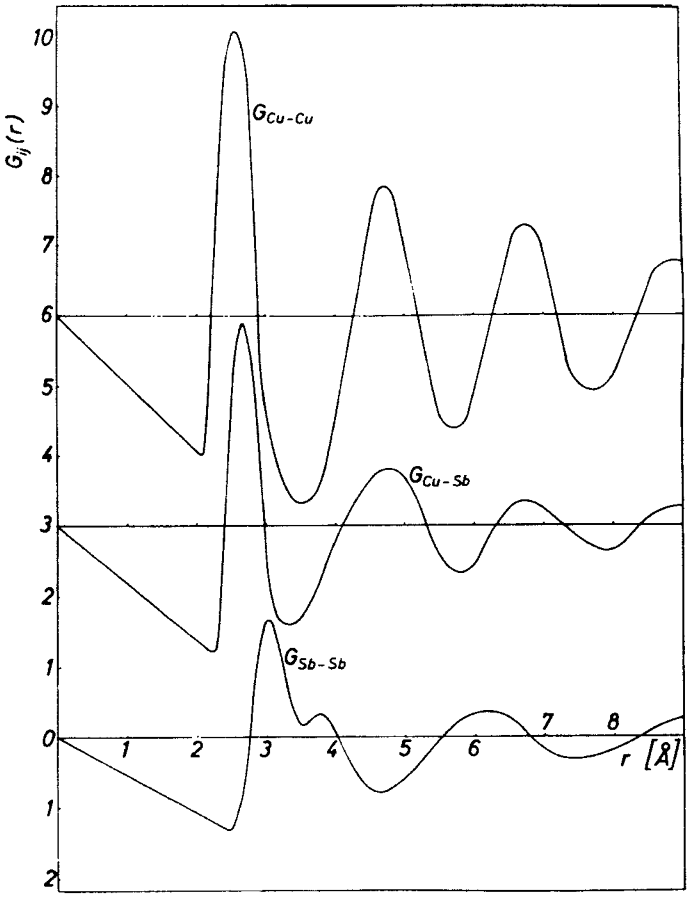

Figure 2. Partial pair correlation functions $G_{ij}(r)$.

A proof for the validity of the assumption of concentration independency of the partial functions is given by the calculation of the partial RDF from the partial interference functions of Fig. 1 using Eq. (5). These partial RDF are composed to total RDF by forming a weighted sum using once for X-rays the atomic numbers of Cu and Sb instead of the scattering factors $f(s)$ and furthermore for neutrons the nuclear coherent scattering amplitudes b. From these RDF the values of r_I shown in Fig. 4 as crosses (X-ray values) and circles (neutron values) are obtained. There is good agreement between these calculated distances r_I and the experimental values (solid line).

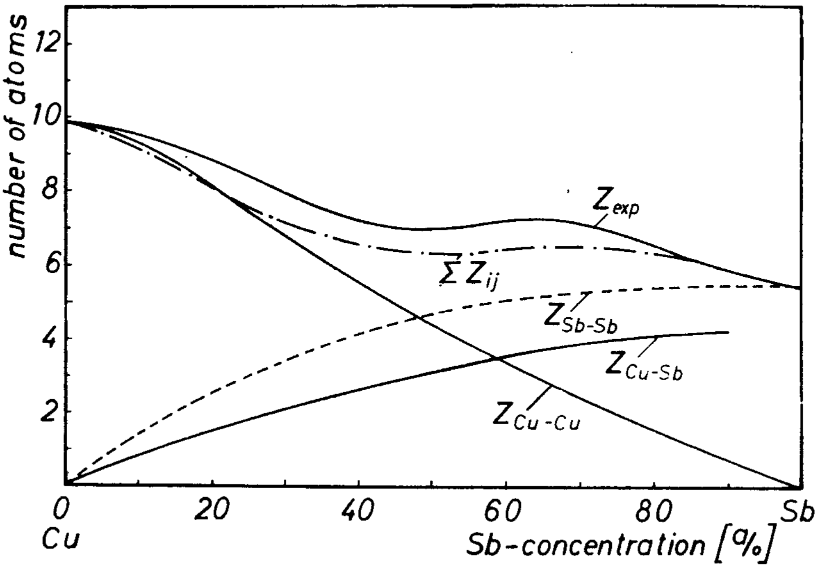

Figure 3. Partial coordination numbers according to Eq. (6); total coordination number z_{exp} from RDF and calculated total coordination number Σz_{ij} according to Eq. (7).

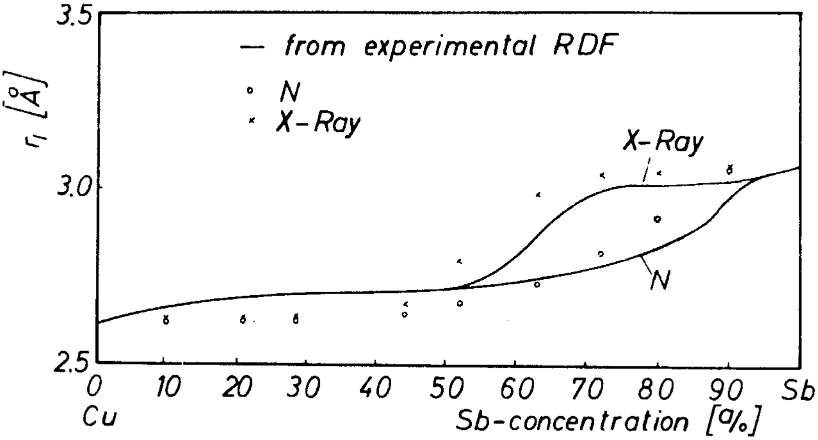

Figure 4. Radius r_I of the first coordination sphere.

According to the experimental values also with the calculated ones a difference in the results from neutron and X-ray diffraction can be remarked for Sb-concentrations larger than 50 at.-%. The accordance between experimental and calculated values is quite good over the whole concentration region.

Another proof for the validity of the partial functions is given by comparison of the total pair correlation functions $G^x(r)$ and $G^N(r)$, obtained from the X-ray and neutron data, with the appropriate curves $\sum w_{ij}^x G_{ij}(r)$ and $\sum w_{ij}^N G_{ij}(r)$ according to Eqs. (7a) and (7b).

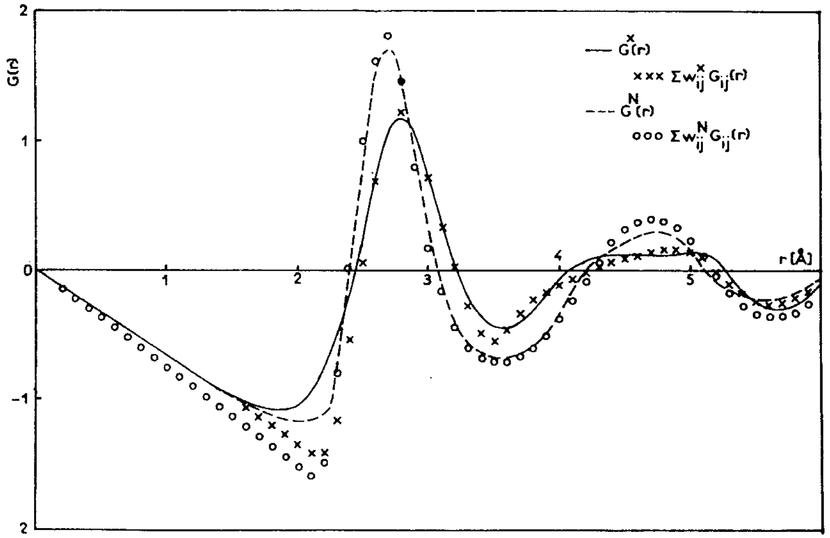

Figure 5. Pair correlation functions of the liquid Cu–Sb alloy containing 63 a/o Sb at 536 °C.

This comparison is done in Fig. 5 for the alloy containing 63 a/o Sb. The total pair correlation functions are given by a solid (X-ray data) and a dashed line (neutron data). There is a marked difference in the shape and position of the first maximum. This was discussed in an earlier work⁽¹⁾ and is also obvious from Fig. 4. It may be noted, that the inherent coordination numbers are not different, because of the varied shape of the first peak.

Marked differences also occur at the second peak, which, however, is not very prominent. Therefore no relation was made between the position of the first and second peaks.

Comparing now the corresponding curves, once $G^x(r)$ and $\sum w^x_{ij} G_{ij}(r)$ (crosses), and furthermore $G^N(r)$ and $\sum w^N_{ij} G_{ij}(r)$ (open circles), a very good agreement can be stated. This proves that the partial pair correlation functions describe exactly the atomic arrangement in this liquid binary alloy. This also can be stated for the whole concentration range of the system Cu–Sb.

As an application of the partial interference functions the electrical resistivity of molten Cu–Sb alloys shall be calculated using the theory of Faber and Ziman.⁽¹⁰⁾ The pseudo potentials used for this purpose were given by Animalu.⁽¹¹,¹²⁾ They are functions of $s/(2k_F)$ with s = length of scattering vector and k_F = length of Fermi-vector for the alloy. Animalu's values U^A_i must be transformed according to

$$U_i = \frac{k_{Fi} \cdot U^A_i}{k_F \cdot \rho_i} \tag{10}$$

into U_i-values, which are then introduced into the Faber–Ziman formula. (ρ_i = atomic density of the element i in the solid state, k_{Fi} = Fermi level of the element i in the solid state). For the

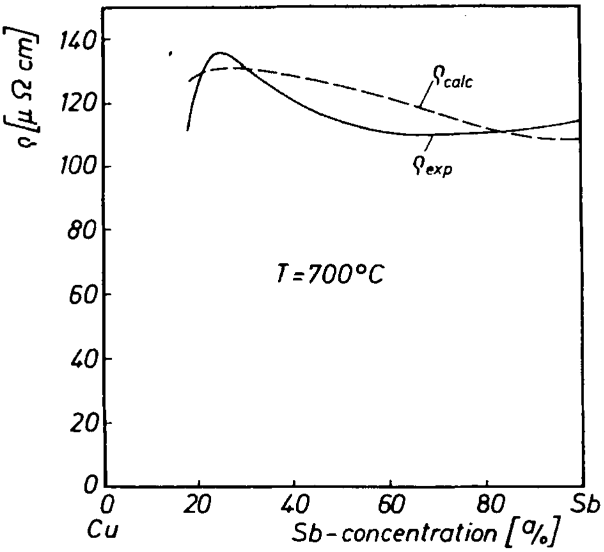

Figure 6. Specific electrical resistivity ρ versus Sb concentration.

calculation of the pseudo potential U_i in the molten state according to Eq. (10) the Fermi-vectors k_F of the molten alloys are needed. To get these values, the mean atomic density ρ_0 of the melt is required, which follows from the measured density.(13) Finally the calculated electrical resistivity for two isotherms (700 and 1100 °C) is presented in the Figs. 6 and 7. These values can be compared with measured values,(14) given as a solid line in the Figs. 6 and 7.

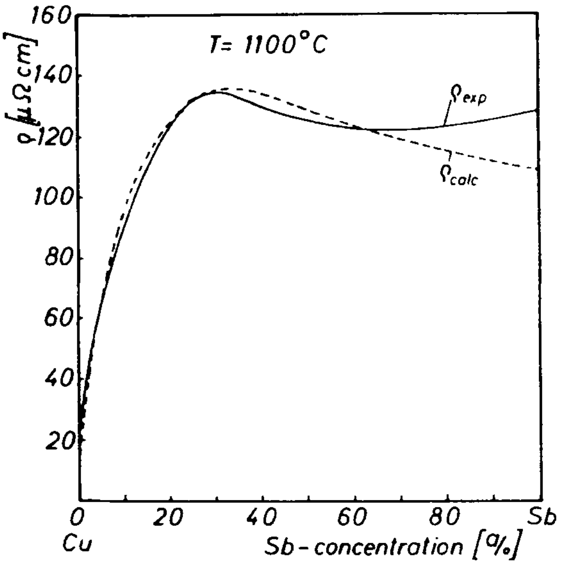

Figure 7. Specific electrical resistivity ρ versus Sb concentration.

The difference between ρ_{calc} and ρ_{exp} is smaller than 10% for the temperature of 700 °C (Fig. 6). Nevertheless, it is obvious that the marked maximum of ρ_{exp} at 25 at.-% Sb and the decrease of ρ_{exp} at higher Sb concentrations to a minimum at the eutectic composition (63 at.-% Sb) is not reproduced by the run of ρ_{calc}.

In Fig. 7 (1100 °C) ρ_{calc} and ρ_{exp} show only deviations smaller than 5% for alloys with up to 63 at.-% Sb. The rise of ρ_{exp} between 60 and 100 at.-% Sb is not realized by ρ_{calc}. The deviation for pure Sb amounts to 15% at 1100 °C, compared with 5% at 700 °C.

All deviations between ρ_{exp} and ρ_{calc} can be explained by the fact that the Faber–Ziman theory is based on the assumption of a molten alloy containing atoms only in statistical distribution.

According to Ref. 10 the thermoelectric power of the molten alloys also can be calculated from the partial interference functions and the pseudopotentials. Since no experimental values exist for the alloys, it is impossible to compare the calculated values given in Fig. 8 for 700 and 1100 °C. The experimental values for the pure metals Cu(15) and Sb(16) are indicated by arrows in Fig. 8. There is good agreement for Sb at 700 °C, however the temperature dependency shows discrepancies. The deviation for molten copper is appreciable, therefore it can be assumed that the calculated values for the thermoelectric power of the alloys fit better for high Sb concentrations.

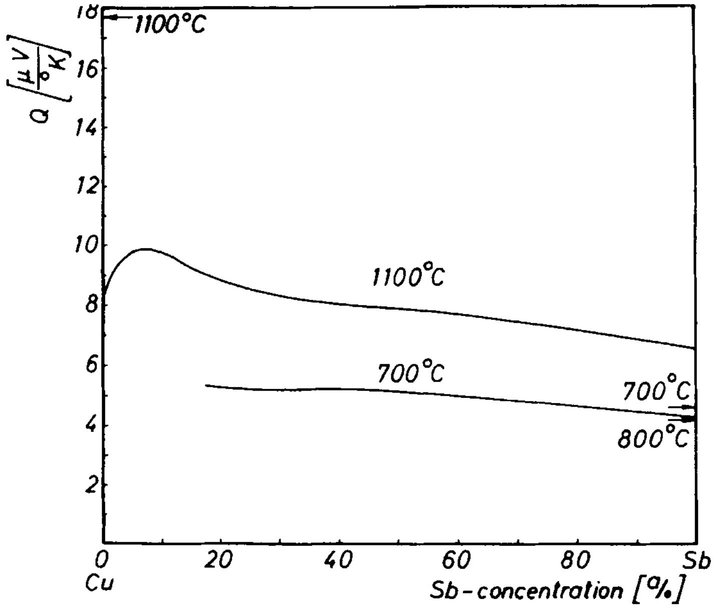

Figure 8. Thermoelectric power Q versus Sb concentration. (The arrows mean experimental values.)

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