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Velocity of Ultrasound in Molten Au-Co Alloys for the Determination of Compressibility and Partial Structure Factors

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The velocity of ultrasound was measured in molten Au-Co alloys containing 0, 10, 20, 27, 30, 40, 50, 60, 70, 80, 90, and 100 at.% Co within the temperature range from 995°C to 1700°C. The temperature coefficient of the velocity versus concentration plot shows a positive deviation from ideal behaviour. The adiabatic compressibility was calculated from the velocity and is discussed. From it the partial structure factors $a_{ij}(0)$ and $S_{kl}(0)$ for zero momentum transfer were obtained. According to these results, the melts of the Au-Co system show a weak tendency to segregation, i.e. they show concentration fluctuations. Between zero and 60 at.% Co these concentration fluctuations correspond to Au-enriched regions and Co-enriched regions, these being present to the same extent. Between 60 and 100 at.% cobalt the influence of Co-enriched regions is greater than that of the Au-enriched regions.

1 INTRODUCTION

Gubanov¹ and Handrich² showed in a theoretical work that ferromagnetism may exist not only in the crystalline state but also in the amorphous or molten states. For example, the existence of amorphous ferromagnetic material could be shown with Au-Fe³ or Au-Co⁴ specimens. Busch and Güntherodt⁵ measured the transition between paramagnetic and ferromagnetic behaviour of Au-Co melts containing 27 at.% Co at a temperature about 20°C above the solidus temperature while cooling down the melt. This transition was confirmed by Alexander *et al.*⁶ by measurements of susceptibility and by Knoll *et al.*⁷ by depolarisation experiments of polarized

neutrons. On the other hand, this transition was not observed at the temperature mentioned by other authors.⁸⁻¹¹

X-ray and neutron diffraction experiments with molten Au-Co-alloys show a slight tendency to segregation.¹² During the present work further information shall be obtained concerning the structure of Au-Co-melts in the following manner: the velocity of ultrasound is measured and the compressibility is deduced. According to Bhatia and Thornton¹³ as well as Turner *et al.*¹⁴ the partial structure factors for zero scattering angle can be calculated by means of isothermal compressibility and the thermodynamic activity. Also, it is possible to deduce a figure which gives a measure of the interaction between nearest neighbour atoms within the melt.

2 THEORETICAL OUTLINE

The theoretical principles are given in a previous paper.¹⁵

3 EXPERIMENTAL DETAILS AND RESULTS

The measurement of the velocity of ultrasound was made using the pulse-echo method, applied to molten metals for the first time by Seemann and Klein.¹⁶ The experiments were done as described in detail in ref.¹⁷ To obtain the rather high temperatures of about 1700°C, a cylindrical heating element made from graphite was used which was slitted three times down to the electrical neutral point and was supplied by three water cooled power supplies. Following Plass,¹⁸ the massive Al₂O₃ cylinder which led the ultrasound from outside the vacuum vessel into the melt was coated to obtain a good contact between this cylinder and the melt. For this purpose thin films of Cr, Co, and Au were evaporated one after the other onto the polished surface of the cylinder, without breaking the vacuum of about 10⁻⁵ Torr. The Cr film provides good contact to the surface of ceramic, the Au film prevents the oxydation of the evaporated films during the installation of the equipment and furthermore forms a good transition to the Au-Co melt. Co finally was added to maintain the Au to Co ratio within the melt.

The velocity of ultrasound is plotted versus temperature for the different Au-Co alloys in Figure 1. The straight lines were obtained using the least-squares method. The parameters for these straight lines are collected in Table 1. Since there was very good contact between Al₂O₃ cylinder and the melt, the standard deviations are rather small for the alloys containing 30, 50, and 80 at.% Co. Therefore, with these alloys it is possible to investigate the temperature dependency u_{ad} in more detail.

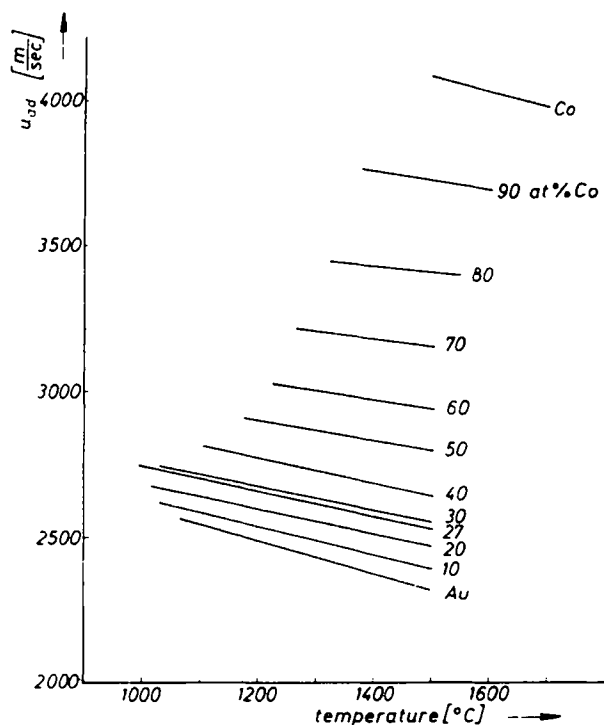


FIGURE 1 Au-Co system: Temperature dependence of the adiabatic velocity of ultrasound.

TABLE 1

Au-Co system: Velocity of ultrasound with standard deviations and temperature coefficients

Cobalt-concentration [at. %]	u_{ad} at melting point [m/sec]	Standard-deviation [m/sec]	Temperature-coeff. du/dT [m/sec°C]
0	2567.5	23	-0.571
10	2621	25	-0.49
20	2679	32	-0.43
27	2753	40	-0.44
30	2747	9	-0.423
40	2818	40	-0.44
50	2912	18	-0.345
60	3028	43	-0.32
70	3215	38	-0.26
80	3446	17	-0.222
90	3767	41	-0.35
100	4084	34	-0.504

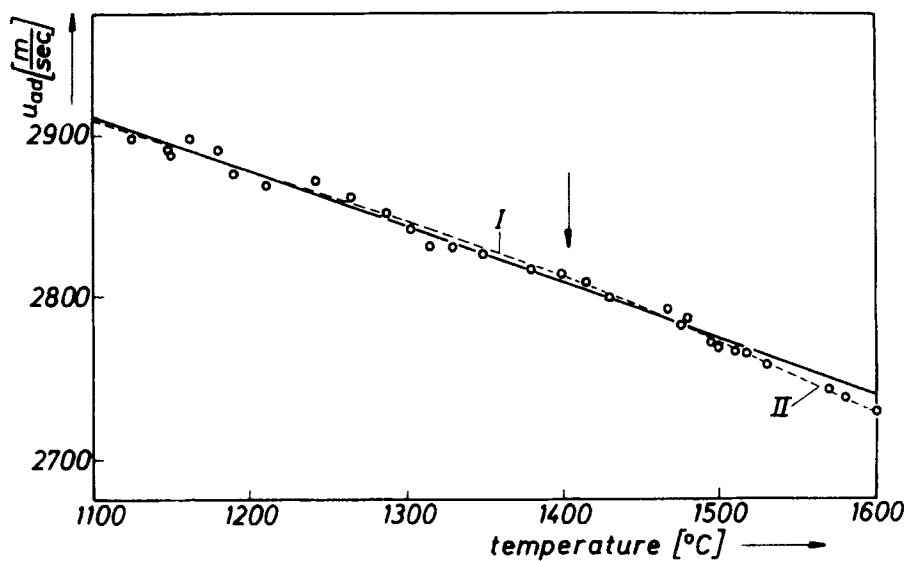


FIGURE 2 Au + 50 at. % Co: Temperature dependence of the adiabatic velocity of ultrasound.

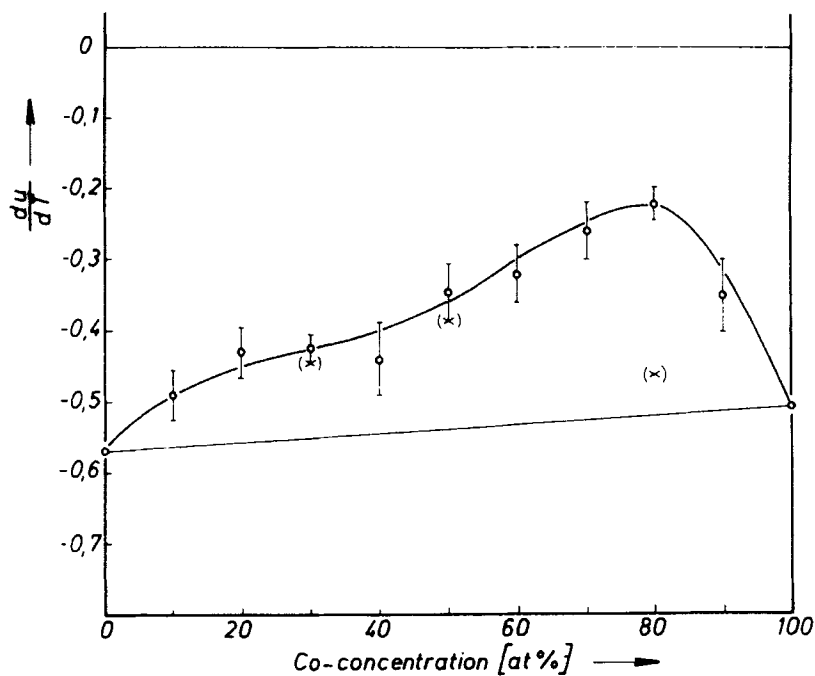


FIGURE 3 Au-Co system: du/dT versus concentration.

Figure 2 shows the data points obtained with the 50 at.% alloy. As can be seen, these points can be fitted by one straight line as in Figure 1 as well as by two straight lines showing a transition region near the arrow indicated.

Figure 3 shows the temperature coefficient of the adiabatic velocity of sound du/dT versus concentration. The temperature coefficients for the $u(T)$ curves composed according to Figure 2 are marked by (\times). According to references^{15,17,19} a change in temperature coefficient means an indication of changes in structure in the temperature range under consideration. With increasing temperature the du/dT curves should approach Raoult's straight line, which represents the ideal behaviour.

Figure 4 shows two isothermes of the velocity of sound versus the concentration.

An estimation of errors performed in reference²⁰ shows the maximum relative error for the determination of the adiabatic velocity of sound to be between 2.5 and 3%, depending on the concentration. Since densities in molten Au-Co alloys are known only for the pure components, the error for the adiabatic compressibility to be determined later will be about 10%.

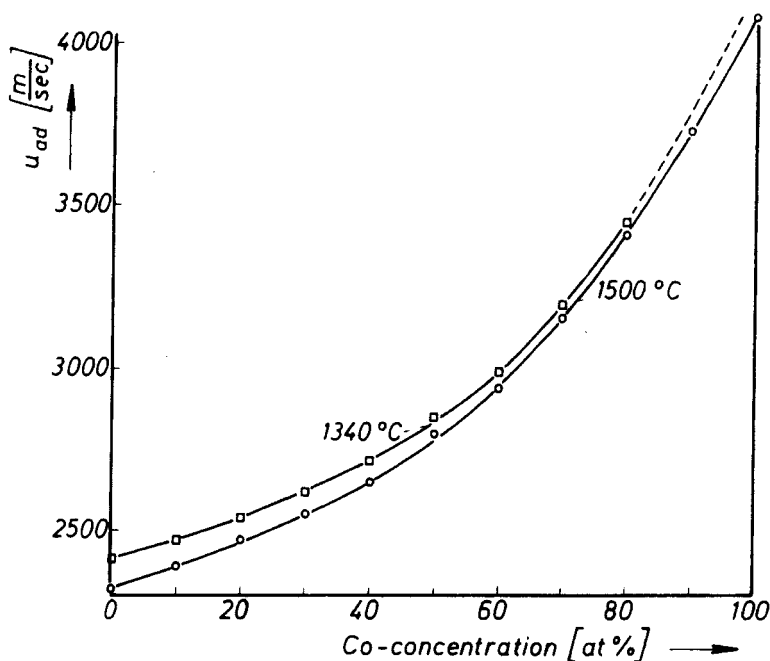


FIGURE 4 Au-Co system: Concentration dependence of the adiabatic velocity of ultrasound at 1340°C and 1500°C.

4 DISCUSSION OF THE RESULTS

A General remarks

The Au-Co phase diagram²¹ shows eutectic behaviour, with the eutectic concentration at 27 at.% Co. The following data, useful for the subdivision of Au-Co melts into Sauerwald's classification, are known: positive enthalpy of mixing,^{23,24} positive deviation from ideal activities,^{23,25} positive excess-entropies and small free energies,²¹ the latter however in solid state at $T = 1150^\circ \text{K}$. Using Sauerwald's criteria the Au-Co-melts behave as partially segregated melts. The stability function of Darken²⁶ shows negative excess stability.

B Comparison of the calculated and measured velocity of sound

For the two pure components Au and Co, the velocity of sound at the melting point can be calculated using the methods of Klein²⁷ and Ascarelli²⁸ (compare also reference¹⁵). The values thus obtained are given in Table 2, which shows good agreement between the measured and calculated velocities for the case of cobalt. As observed already for Ag and Cu²⁸ there is a rather large deviation between the value calculated using the Ascarelli method and the experimental value for Au. In these cases Klein's method seems to be more suitable. By Ascarelli this behaviour was explained by an overlap of electron shells of neighbouring atoms, which would lead to an exchange energy for Ag, Cu, and Au which would yield higher values of the velocity of ultrasound.

C Change in the velocity of ultrasound during melting

Examination of the ultrasonic velocity data for elements in the solid and liquid state collected in reference^{28,29} reveals that the ratio u (solid)/ u (liquid) is between 1.1 and 1.2 at the melting point. The values of the ultrasonic velocity in Au as well as in Co melts, measured for the first time in this work, are shown in Figure 5 in comparison with the solid state values given in reference.²⁹

TABLE 2
Velocity of ultrasound in Au and Co melts according to various theories

	u_{Klein} [m/sec]	u_{Asc} [m/sec]	u_{exp} [m/sec]	u_{Klein}	u_{Asc}
				u_{exp}	u_{exp}
Au	2218	1605	2567.5	0.87	0.63
Co	2930	3950	4084	0.96	0.97

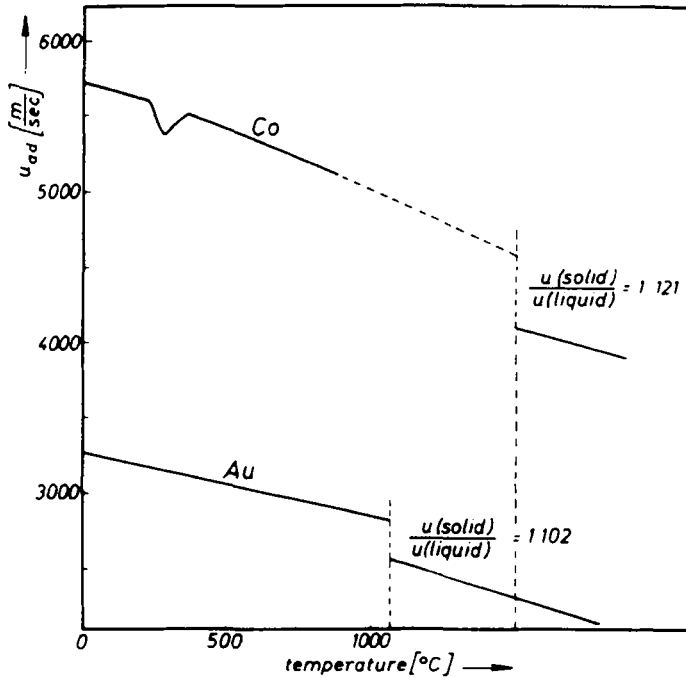


FIGURE 5 Temperature dependence of the velocity of ultrasound in Au and Co.

D Adiabatic compressibility

The adiabatic compressibility β_{ad} can be obtained from the adiabatic velocity of ultrasound u_{ad} from

$$\beta_{ad} = \frac{1}{\rho \cdot u_{ad}^2} \quad (1)$$

ρ being the macroscopic density.

Since in the literature the density is known for the pure components only (Au in ref.³⁰ and Co in ref.³¹), the densities of the alloys must be calculated on the basis of Vegard's law. The error in density caused by this method amounts from 1 to 5%. The error in adiabatic compressibility then should be about 5 to 10%, whereas the error for the isothermal compressibility will be larger, since for its calculation either the coefficient of volume expansion and the specific heat c_p or the ratio c_p/c_v are necessary.

The velocity data from Table 1 were used to calculate the adiabatic compressibility which is plotted versus temperature in Figure 6. The curves show a slight deviation from linearity especially for small Co concentrations.

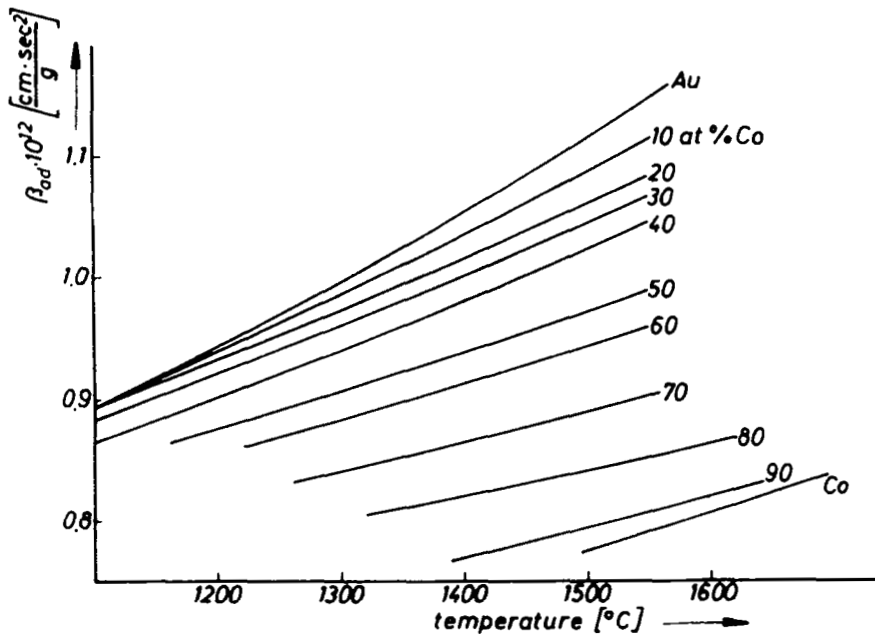


FIGURE 6 Au-Co system: Temperature dependence of the adiabatic compressibility.

In Figure 7 the isotherme of adiabatic compressibility at 1500°C for the Au-Co system is plotted versus concentration, together with the corresponding curves for the Al-Mg¹⁷ (1000°C), Al-Sn¹⁷ (650°C), Bi-Cu¹⁵ (1100°C), Bi-Mg³² (832°C), Cu-Sn¹⁴ (1100°C), Mg-Sn¹⁷ (800°C), and Pb-Sn³⁵ (550°C) systems. The plots for the Au-Co, the Pb-Sn, and the Al-Sn systems are linear. The curves for the Bi-Mg system deviate from this line to higher values and the others to lower values. The discrepancies in compressibility of the pure components should be stressed as well as the fact that no well defined relationship seems to exist between the curves shown in Figure 2 and the structure of the corresponding melts.

E Temperature dependence of the total interference function $I(0)$

The interference function $I(0)$ for zero scattering angle can be calculated on the basis of eqn. (2).

$$I(0) = \rho_0 \cdot k_B \cdot T \cdot \beta_T \quad (2)$$

from the isothermal compressibility β_T , the Boltzmann constant k_B , and the number density ρ_0 for a certain temperature T .³⁴ The results for Au and Co are presented in Figure 8.

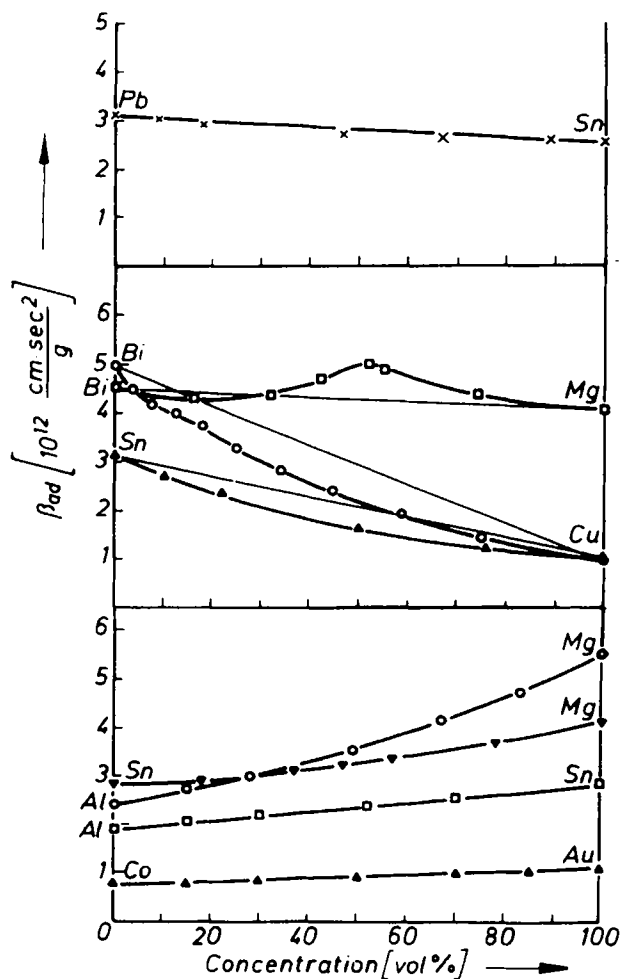


FIGURE 7 Concentration dependence of the adiabatic compressibility in various systems.

These values can be compared directly with values obtained from scattering experiments. Some reasons for the discrepancies between calculated and experimental values were discussed by Hezel.³⁵

F Partial structure factors for scattering angle zero

The compressibility of chapter 4.D, the density averaged from the pure components, from this the partial molar volumes and the activities of ref.²³ were used for the calculation of the partial structure factors $a_{ij}(0)$ using Mc Alister and Turner³⁶ method and for the partial factors $S_{CC}(0)$, and $S_{NC}(0)$

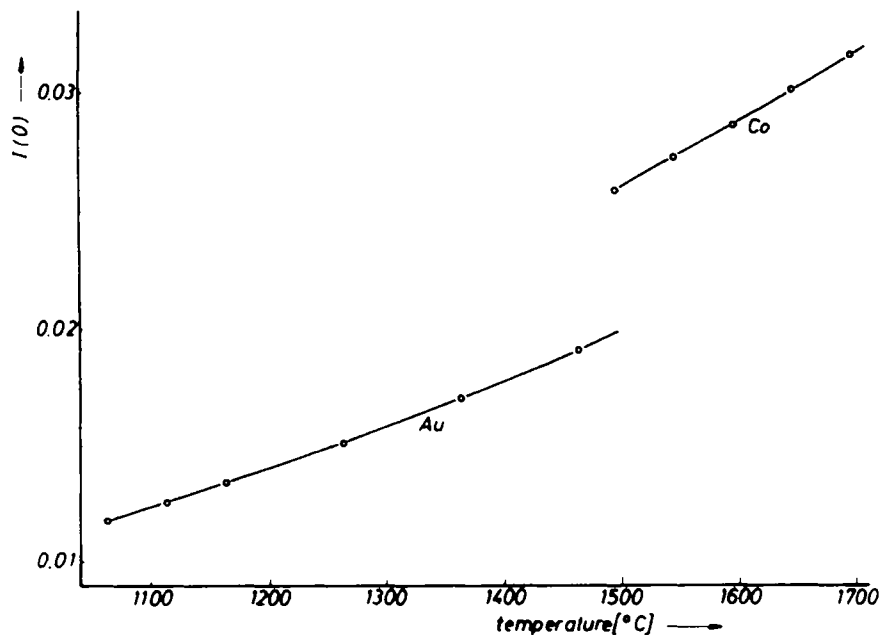


FIGURE 8 Temperature dependence of $I(0)$ for Au and Co.

using the Bhatia and Thornton¹³ method. Since the activities are known only for the temperature interval 1250° C to 1350° C, the partial structure factors could be obtained for melts containing less than 80 at. % Co. In Figure 9 the partial structure factors $a_{ij}(0)$ are plotted versus concentration. Obviously, the functions $a_{ij}(0)$ vary considerably with concentration. The concentration dependence can be caused on the one hand by the considerable difference ($V_{Au} - V_{Co}$) in atomic volume of either species, which for the Au-Co system amounts 1.5 to 6.2 cm³. On the other hand differences in the interaction between i - j pairs and i - i pairs may cause this behaviour. In the following it will be shown how the influence of the pair interaction can be evaluated. According to Turner *et al.* (14) the quantity ΔN_j is defined by Eqn. (3)

$$\Delta N_j = c_j [a_{ij}(0) - a_{jj}(0)] \quad (3)$$

ΔN_j is the difference between the total numbers of j -atoms surrounding an i -atom and the total number of j -atoms surrounding a j -atom.

A model¹⁴ which considers the different atomic volumes only, disregarding the interaction between the species, allows one to calculate a quantity ΔN_j^{calc} . The resulting quantity $\Delta N_j'$ defined by Eqn. (4)

$$\Delta N_j' = \Delta N_j - \Delta N_j^{\text{calc}} \quad (4)$$

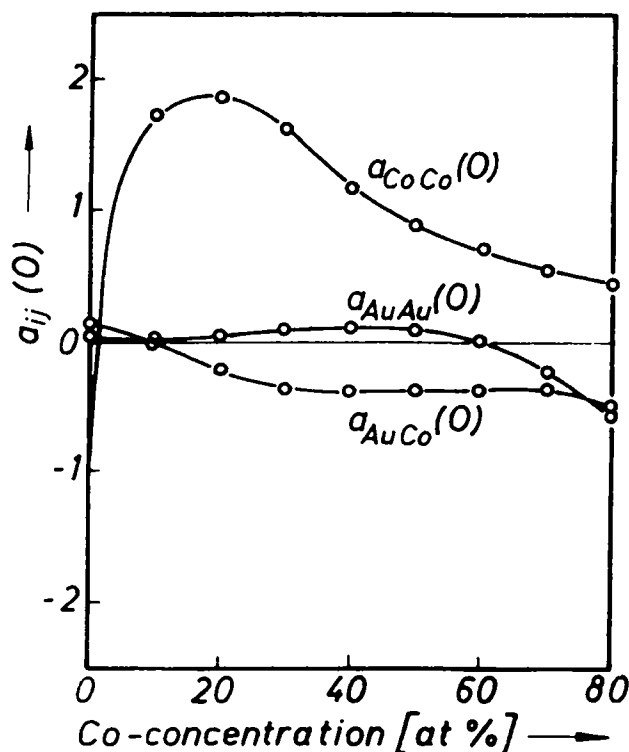


FIGURE 9 Au-Co system: Concentration dependence of the partial structure factors $a_{ij}(0)$ at 1340°C.

then describes the effect on local structure resulting from the interaction energy between the two components. By means of $\Delta N'_i$ it is possible to place the melts into one of the following classes

$$\Delta N'_i \begin{cases} > \\ = \\ < \end{cases} 0 \text{ corresponds to } \begin{cases} \text{preference for dissimilar atoms} \\ \text{statistical distribution} \\ \text{preference for similar atoms} \end{cases}$$

The composition dependence of $\Delta N'_{Au}$ and $\Delta N'_{Co}$ at $T = 1340^\circ\text{C}$ is shown in Figure 10. The values of $\Delta N'_{Au}$ and $\Delta N'_{Co}$ are slightly negative over nearly the whole composition range, indicating that in Au-Co melts the Au-Au as well as the Co-Co correlation are stronger than the Au-Co correlation. $\Delta N'_{Co}$ is more negative than $\Delta N'_{Au}$ over the whole range. However, it is to be emphasized that this effect is of an order of magnitude smaller than in the Bi-Cu system,¹⁵ which shows strong effects of self-correlation, i.e. a tendency to segregation. In Figure 11 the partial functions $S_{CC}(0)$, $S_{NN}(0)$ and $S_{NC}(0)$ are

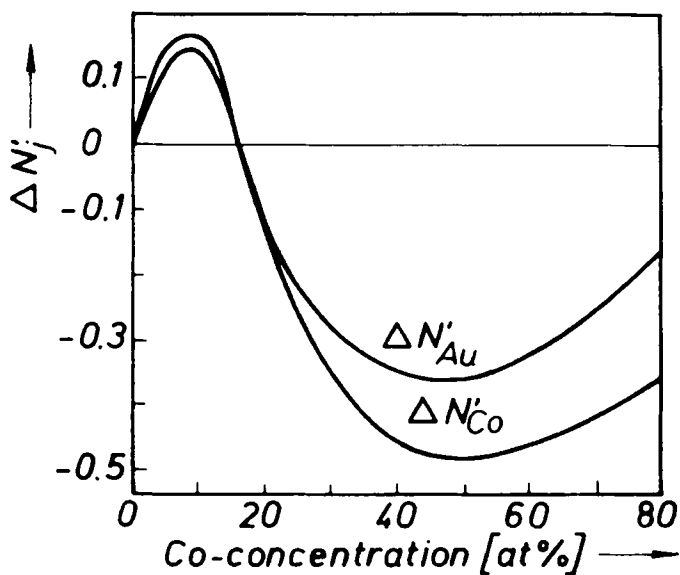


FIGURE 10 Au-Co system: Concentration dependence of $\Delta N'_{Au}$ and $\Delta N'_{Co}$ at 1340°C.

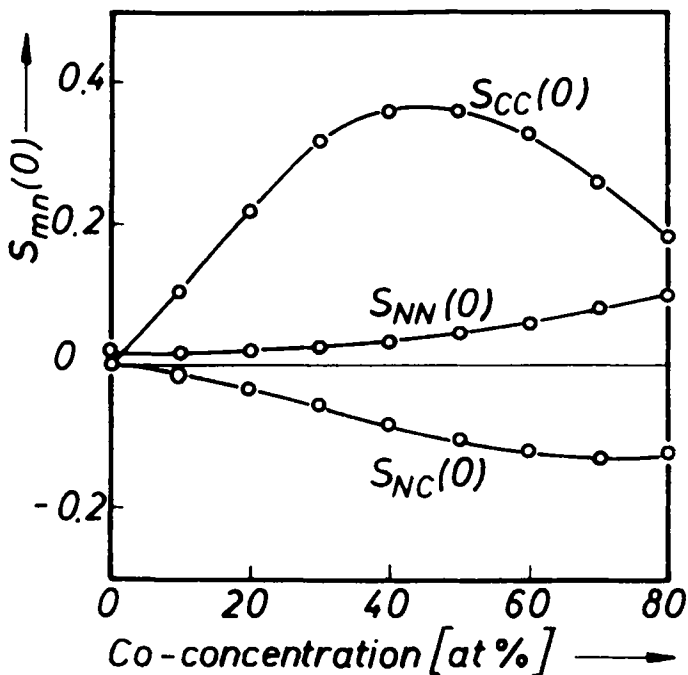


FIGURE 11 Au-Co system: Concentration dependence of $S_{CC}(0)$, $S_{NN}(0)$, and $S_{NC}(0)$ at

plotted versus composition. $S_{CC}(0)$ exhibits a broad maximum in the range from 30 to 60 at. % Co, which means, that alloys within this composition range show considerable fluctuations in concentration. Over the whole concentration region $S_{NN}(0)$ doesn't exceed the value of $S_{NN}(0)$ for the pure components, which is given by $\rho_0 K_B T \beta_T$.

This means that the effect of the difference between the molar volumes on the partial quantities is rather small. However, it should be mentioned that the use of averaged density values instead of experimental ones may cause this behaviour. Comparison of the Au-Co system with the system Bi-Cu, where a marked tendency for Cu-Cu correlation was found, shows that Au-Co is a system with only a weak tendency to segregation.

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