# Structure and Compressibility of Au-Co Melts

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(Z. Naturforsch. **31 a**, 1348—1353 [1976]; received September 7, 1976)

Alloys of the Au-Co system containing 0, 20, 27, 30, 32, 36, 41, 55, 70, and 100 at.% Co were investigated at temperatures between 10 and 20 °C above the liquidus by means of thermal neutron (wavelength 1.20 Å) and X-ray (Mo-K$\alpha$) diffraction. The interference functions show no additional maxima or deformations. Radial distribution functions were obtained and from these the coordination numbers $N^{\mathrm{I}}$ and nearest neighbour distances $r^{\mathrm{I}}$ were obtained and plotted versus the concentration together with the curves to be obtained for the ideal case and the case of total segregation. With both plots the experimental values lie between these curves thus indicating a tendency to segregation within these melts.

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 adiabatic compressibility was calculated from the velocity. From it the partial structure factors $a_{ij}(0)$ and $S_{kl}(0)$ for zero momentum transfer were obtained. According to the results, the melts of the Au-Co system show a weak tendency to segregation.

Thus it could be proved by two independent methods, that Au-Co melts show a tendency to segregation.

Busch and Güntherodt[1] 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 and Kraft[2] by measurements of susceptibility and by Knoll et al.[3] by depolarization experiments of polarized neutrons. On the other hand, this transition was not observed at the temperature mentioned by Hildebrand[4], Nakagawa[5], Menth and Bagley[6], and Wachtel and Kopp[7].

Regarding the discrepancies in the magnetic behaviour of Au-Co melts it is evident, that more details concerning these melts should be known. The present work was done to obtain more information on the mutual arrangement of atoms within the Au-Co melts. One hint was given by Predel and Zehnpfund[8] who indicated that the enthalpy of mixing should be +1 kcal/Mol, thus indicating a tendency of segregation. The section of the present work concerned with diffraction experiments is based on the experimental results obtained by Reule[9]. The method of X-ray diffraction in reflection and the method of neutron diffraction in transmission were used to supplement one another. Thus it is possible to detect and delete systematic errors, since both methods demand different correction methods. On the other hand, the ratio of scattering cross sections of gold and cobalt is three for X-rays and for neutrons, so that the interference functions are directly comparable. The results obtained by diffraction methods will be completed by partial structure factors for zero scattering angle which are deduced from ultrasound velocities via compressibilities.

## 1. Diffraction Experiments

### *1.1. Theoretical Fundamentals*

For the evaluation of the coherent scattering intensities $I_{\mathrm{coh}}(s)$ the Kaplow, Strong and Averbach[10] method, which uses the following equation, was used

$$I_{\mathrm{coh}}(s) = \langle f^2 \rangle + \langle f \rangle^2 \int_0^\infty 4\pi r (\varrho - \varrho_0) \frac{\sin s r}{s r} \, \mathrm{d}r \qquad (1)$$

with $s = 4\pi \sin \Theta / \lambda$,

$\Theta$ = scattering angle,
$\lambda$ = wavelength,
$f_i$ = scattering length of atoms of kind $i$ for X-rays,
$\varrho$ = local number density,
$\varrho_0$ = mean number density.

The interference function $I(s)$ is calculated using Eq. (2):

$$I(s) = [I_{\mathrm{coh}}(s) - \langle f^2 \rangle + \langle f \rangle^2] / \langle f \rangle^2 \,. \qquad (2)$$

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From the interference function, the pair correlation function $G(r)$, which has the following meaning, may be obtained by taking the Fourier transform:

$$G(r) = 4\pi r(\varrho - \varrho_0)\,. \tag{3}$$

### *1.2. Preparation of Specimens and Performance of Diffraction Experiments*

The specimens were prepared in a vacuum induction furnace from gold (99.999%) and cobalt (99.990%). For neutron diffraction experiments, flat specimens with a thickness of 2.5 to 3.5 mm were prepared.

#### 1.2.1. X-ray Diffraction Experiments

The X-ray experiments were performed according to the reflection method, as described by Bühner and Steeb [11] using Mo-K$\alpha$ radiation. The variation in temperature was about ±10 °C. A flat surface was obtained as a result of the large container area of about $25 \times 35$ mm$^2$. The container consisted of $Al_2O_3$ or of carbon coated with tungsten. The mean relative deviation amounted to 3% at $s = 3$ Å$^{-1}$ and to 5% at the maximum $s$ value of 8.5 Å$^{-1}$.

The measured intensities were corrected for background, polarization, absorption, and Compton scattering. The corrected coherent intensity was normalized to electron units using the Krogh-Moe [12] method.

#### 1.2.2. Neutron Diffraction Experiments

The neutron diffraction experiments were done according to the transmission method described by Knoll and Steeb [13]. However, the absorption correction had to be changed according to Sagel [14], since in the present case flat containers of $Al_2O_3$ were used. This was necessary, since gold shows a rather large absorption cross section for thermal neutrons. The variation in temperature was about ±5 °C. The neutron diffractometer used is installed at the FR2 research reactor at the Karlsruhe Nuclear Research Center. The wavelength of the neutrons used was 1.2 Å.

The measured intensities were corrected for background scattering, absorption (according to Sagel [14]), inelastic scattering arising from spin incoherency, and magnetic scattering (according to Reule [9]). A correction according to Placzek [15] and a correction for multiple scattering according to Vineyard [16] could be neglected in the present case of Au-Co melts since the attenuation coefficient for multiple scattering only was 0.1% of the attenuation coefficient for absorption and since the Placzek correction was only maximum 1% of the incoherently scattered intensity. The coherent scattered intensity thus obtained was normalized according to Krogh-Moe [12].

The mean number density $\varrho_0$ from Eq. (1) is calculated according to Eq. (4)

$$\varrho_0 = \frac{L\,D\,10^{-24}}{M}\ [\text{number/Å}^3] \tag{4}$$

with $L$ = Avogadro's number, $D$ = density, $M$ = atomic weight.
The densities of molten Au-Co are not known, thus they were calculated by linear interpolation, with respect to volume concentration, between the densities of molten gold and molten cobalt reported by Gebhardt and Dorner [17] and by Lucas [18]. The scattering lengths were taken for gold and cobalt from the papers of Cromer and Waber [19] and Cromer and Mann [20]. They were corrected for dispersion according to Cromer [21]. For neutron diffraction the scattering lengths for gold and cobalt were taken from the papers of Hughes and Schwartz [22] and Moon [23].

### *1.3. Results and Discussion*

#### 1.3.1. Interference Functions

In the Au-Co system intensity curves were measured by means of neutron diffraction as well as X-ray diffraction from the pure components and from alloys with nine different concentrations at temperatures just above the liquidus line.

From the intensity curves interference functions were obtained using Equation (2). Some of the curves obtained by X-ray diffraction are shown in Figure 1. The interference functions show typical shapes. No anomalies can be observed. The first maximum shows a slight assymetry, since the low $s$-value side of the maximum is a little steeper than the high $s$-value side.

The curves obtained by neutron diffraction scarcely differ from those shown in Figure 1. The difference between the curves amounts to the estimated error of about 3 to 5% at $s = 3.5$ Å$^{-1}$. However, at $s = 3$ Å$^{-1}$ the difference is about 10%, thus indicating some systematic error. This can be explained by the fact that for small scattering angles in the reflection experiment the accuracy of the intensity measurement is not as high as for the transmission experiment. For further evaluation mean values were used.

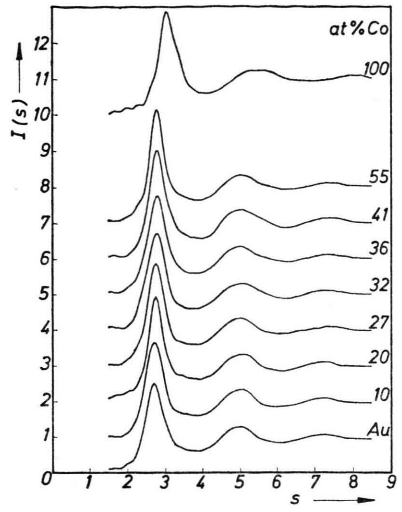

Fig. 1. Interference functions (X-rays).

### 1.3.2. Pair Correlation Function

The pair correlation function obtained by taking the Fourier transform of the interference functions of Fig. 1 are presented in Figure 2. They were calculated using an integration length of $s_{\max} = 8\,\text{Å}^{-1}$ and they show the shape typical for metallic melts. The curves obtained by neutron diffraction are in good agreement with those shown in Figure 2.

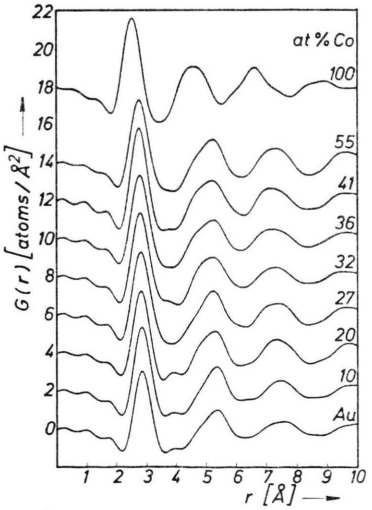

Fig. 2. Pair correlation functions (X-rays).

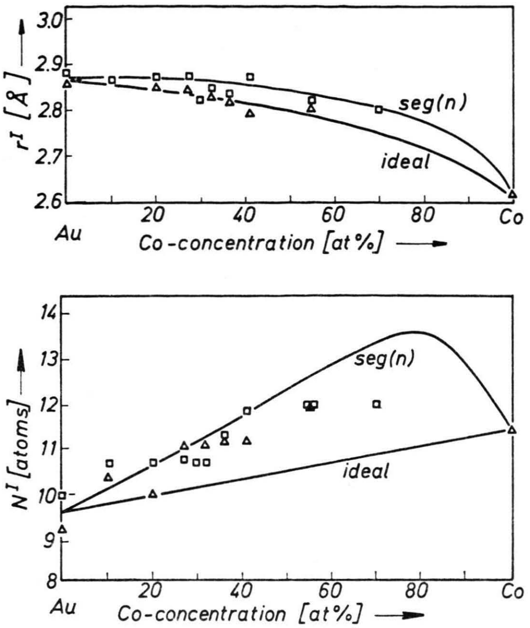

Fig. 3. a) Nearst neighbour distance $r^{I}$,
b) coordination number $N^{I}$,
(□ ≙ neutron diffraction; △ ≙ X-ray diffraction).

### 1.3.3. Nearest Neighbour Distance $r^{\mathrm{I}}$

The pair correlation functions yield the nearest neighbour distances $r^{\mathrm{I}}$, which are plotted versus concentration in Fig. 3 a together with the curve for the ideal case, which was calculated using Eq. (5 a) (see Lamparter et alii [24]).

$$r^{\mathrm{I,st.}} = \frac{c_1^2\, b_1^2\, r_{11}^{\mathrm{I}} + c_2^2\, b_2^2\, r_{22}^{\mathrm{I}} + 2\, c_1\, c_2\, b_1\, b_2\, r_{12}^{\mathrm{I}}}{(c_1\, b_1 + c_2\, b_2)^2}\,. \tag{5 a}$$

Figure 3 a furthermore contains the curve for total segregation, which was calculated using Eq. (5 b) (see Lamparter et alii [24]).

$$r^{\mathrm{I,seg.}} = \frac{c_1\, b_1^2\, N_1^{\mathrm{I}}\, r_{11}^{\mathrm{I}} + c_2\, b_2^2\, N_2^{\mathrm{I}}\, r_{22}}{c_1\, b_1^2\, N_1^{\mathrm{I}} + c_2\, b_2^2\, N_2^{\mathrm{I}}}\,, \tag{5 b}$$

$c_i$ atomic fraction of atoms of kind $i$, $b_i$ scattering length of atoms of kind $i$ for thermal neutrons, $r_{ij}^{\mathrm{I}}$ nearest neighbour distance between an $i$- and $j$-atom, $N_i^{\mathrm{I}}$ coordination number of pure element $i$.

It should be mentioned that the shape of the curves calculated according to Eqs. (5 a) and (5 b) is the same for X-rays and neutrons. Therefore, the data points obtained by the two methods may be plotted in the same diagram. The mean error for the determination of $r^{\mathrm{I}}$ is about ± 0.03 Å (see Reule [9]). It follows clearly from Fig. 3 a that the melts of the Au-Co system show a tendency to partial segregation.

### 1.3.4. Coordination Number $N^{\mathrm{I}}$

The $G(r)$ curves of Fig. 2 yield atomic distribution curves $4\pi r^2 \varrho(r)$. From the first maximum of these curves in each case the coordination number $N^{\mathrm{I}}$ was obtained by the following method: Tangents were drawn at the lower $r$-value side and at the higher $r$-value side of the maximum. These tangents yielded intersections with the abscissa and thus a well defined area below the first maximum was obtained which corresponds to the coordination number. The coordination numbers are plotted versus concentration in Fig. 3 b together with a straight line, which represents the ideal case and a curve, which represents the case of total segregation and which was calculated using Eq. (6) (see Lamparter et al. [24])

$$N^{\mathrm{I,\,segr.}} = \frac{c_1\, b_1^2\, N_1^{\mathrm{I}} + c_2\, b_2^2\, N_2^{\mathrm{I}}}{\langle b \rangle^2}\,. \tag{6}$$

Equation (6) yields the same curve for X-rays and for neutrons. Therefore, the results from both kinds of radiation may be plotted in the same diagram. The mean error for the coordination numbers is ± 0.4 atoms (see Reule [9]). It follows clearly from Fig. 3 b that the melts of the Au-Co system show a tendency to partial segregation.

## 2. Ultrasound Experiments

The theoretical principles of ultrasound experiments are given in a previous paper by Ebert et alii [25].

### 2.1. *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 [26]. The experiments were done as described in detail by Maier and Steeb [27]. To obtain the rather high temperatures of about 1700 °C, a cylindrical heating element made from graphite was used.

Following Plass [28] the massive $Al_2O_3$ cylinder which led the ultrasound from outside the vacuum vessel into the melt was coated with thin films of Cr, Co and Au to obtain good contact.

The velocity of ultrasound is plotted versus temperature for the different Au-Co alloys in Figure 4. The straight lines were obtained using the least-squares method.

An estimation of errors performed according to Bek [29] 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%.

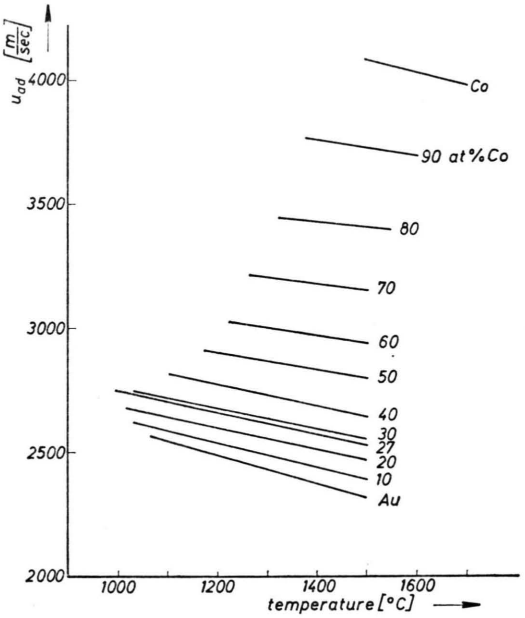

Fig. 4. Temperature dependency of the adiabatic velocity of ultrasound.

### 2.2. *Adiabatic Compressibility*

The adiabatic compressibility $\beta_{\mathrm{ad}}$ can be obtained from the adiabatic velocity of ultrasound $u_{\mathrm{ad}}$ from Eq. (7):

$$\beta_{\mathrm{ad}} = 1/D\, u_{\mathrm{ad}}^2\,. \tag{7}$$

Since to data the densities were only measured for the pure components in the molten state (Au according to Gebhardt and Dorner [17], Co according to Steinberg [30] or Lucas [18], respectively) the densities of the alloys were calculated by linear interpolation, with respect to volume concentration, between the densities of the pure components. The error in density caused by this method amounts to from one up to five percent. The error for the determination of the adiabatic compressibility then should be about 5 to 10%. The velocity of Fig. 4 was used to calculate the adiabatic compressibility which is plotted versus concentration in Figure 5. The curves show a slight deviation from linearity, especially for small concentrations.

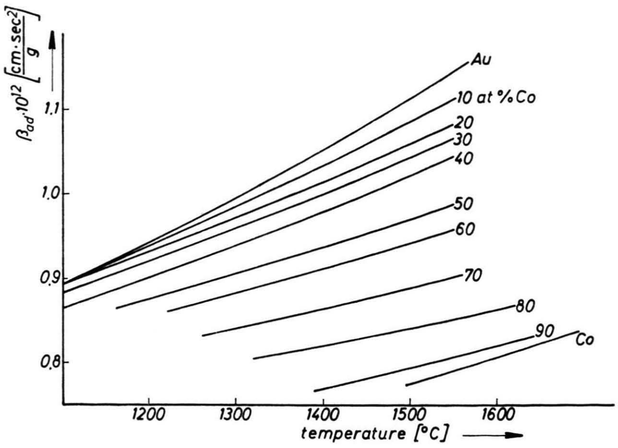

Fig. 5. Temperature dependency of the adiabatic compressibility.

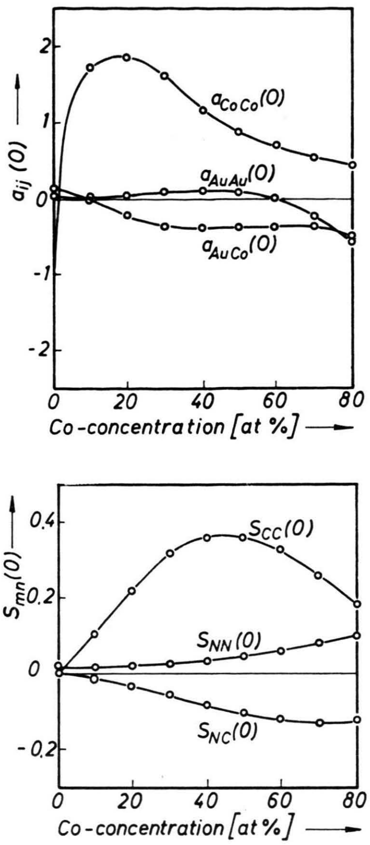

Fig. 6. a) Concentration dependency of the partial structure factors $a_{ij}(0)$ at 1340 °C. b) concentration dependency of $S_{CC}(0)$, $S_{NN}(0)$, and $S_{NC}(0)$ at 1340 °C.

### *2.3. Partial Structure Factors for Zero Scattering Angle*

The compressibility of Fig. 5, the density averaged from the pure components, and the activities according to Wang and Toguri [31] were used for the calculation of the partial structure factors $a_{ij}(0)$ using the McAlister and Turner [32] method and for the partial factors $S_{CC}(0)$, $S_{NN}(0)$, and $S_{NC}(0)$ using the Bhatia and Thornton [33] 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 Fig. 6 a the partial structure factors $a_{ij}(0)$ are plotted versus concentration. Obviously, the functions $a_{ij}(0)$ vary considerably with concentration. This concentration dependency 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. This latter influence can be evaluated according to Turner et alii [34]. They define a quantity $N_j$ as in Eq. (8):

$$\Delta N_j = c_j \{a_{ij}(0) - a_{jj}(0)\} . \tag{8}$$

$\Delta N_j$ is the difference between the total number of $j$-atoms surrounding an $i$-atom and the total number of $j$-atoms surrounding a $j$-atom.

A model according to Turner et al. [34] which considers the different atomic volumes only yields a quantity $\Delta N_j^{\text{calc}}$. The resulting quantity

$$\Delta N_j' = \Delta N_j - \Delta N_j^{\text{calc}} \tag{9}$$

then describes the effect on local structure resulting from the interaction energy between the two components.

$$\Delta N_j' \begin{Bmatrix} > \\ = \\ < \end{Bmatrix} 0$$

$$\text{corresponds to} \begin{cases} \text{preference for dissimilar atoms} \\ \text{statistical distribution} \\ \text{preference for similar atoms.} \end{cases}$$

The values of $\Delta N'_{Au}$ and $\Delta N'_{Co}$ obtained during the present work are slightly negative over nearly the whole composition range, indicating that in Au-Co melts the Au-Au as well as the Co-Co correlations 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 published by Ebert et al. [25]

which shows strong effects of self-correlation, i. e., a tendency to segregation.

In Fig. 6b the partial functions $S_{CC}(0)$, $S_{NN}(0)$, and $S_{NC}(0)$ are 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 $\varrho_0 k_B T \beta_T$ and amounts to $10^{-2}$. 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 in the molten state.

Comparing the results of X-ray and neutron diffraction on the one hand and the results of compressibility measurements on the other, one can state, that all these methods reveal a tendency for segregation with Au-Co melts.

This tendency for segregation could lead to the formation of segregated zones containing for example Co-atoms only. If furthermore within these arrangements some kind of spin ordering could occur, then in this way some kind of ferromagnetic behaviour mentioned in the introduction could be well explained.

*Acknowledgements*

Thanks are due to the Deutsche Forschungsgemeinschaft, to the Gesellschaft für Kernforschung, Karlsruhe, and to the Recheninstitut of the University of Stuttgart.

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