

PARTIAL STRUCTURE FACTOR OF LIQUID GOLD-COBALT ALLOYS

by R. V. GOPALA RAO and D. SEN, *Department of Physical Chemistry,
Jadavpur University, Calcutta 700 032*

(Received 21 August 1978)

Partial structure factors as also number-number, concentration-concentration and number-concentration structure factors (as defined by Bhatia & Thornton, 1970) have been calculated for liquid Gold-Cobalt alloys at various concentrations. The calculations involve simple assumptions and the authors have tacitly assumed that no compound formation takes place between the components of the alloy as suggested by Waseda and Tamaki (1977).

INTRODUCTION

The authors have recently shown (Rao & Sen 1976 *a, b*; 1977 *a, b*) that the structural properties of liquid metals can be explained satisfactorily on the basis of a simple perturbation treatment of Percus-Yevick equation. We now like to extend this treatment to the calculation of partial structure factor, $S_{ij}(k)$ of a simple alloy of liquid gold and cobalt which do not form any compound as have been claimed by Waseda and Tamaki (1977). We also propose to calculate the number-number, concentration-concentration and number-concentration structure factors, $S_{NN}(k)$, $S_{CC}(k)$ and $S_{NC}(k)$ respectively, as defined by Bhatia and Thornton (1970) for these alloys.

THEORY

For binary mixtures, we assume that the direct correlation function, $C_{ij}(r)$ is given by :

$$\begin{aligned} C_{ij}(r) &= C_{ij}^0(r), \quad 0 < r \leq \sigma_{ij} \\ &= -\phi_{ij}(r) / K_B T = \epsilon_{ij} / K_B T, \quad \sigma_{ij} < r < A_{ij} \sigma_{ij} \\ &= 0, \quad r > A_{ij} \sigma_{ij} \end{aligned} \quad \dots (1)$$

Here $C_{ij}^0(r)$ stands for the hard-sphere solution of Percus-Yevick equation for binary liquid mixtures by Lebowitz (1964), σ_{ii} , ϵ_{ii} and A_{ii} stand respectively for hard sphere diameter, depth and breadth of the square well used for the species i . The mixed parameters may be defined as follows :

$$\begin{aligned} \sigma_{ij} &= (\sigma_{ii} + \sigma_{jj})/2 \\ \epsilon_{ij} &= (\epsilon_{ii} + \epsilon_{jj})^{1/2} \\ A_{ij} &= (A_{ii} \sigma_{ii} + A_{jj} \sigma_{jj}) / (\sigma_{ii} + \sigma_{jj}) \end{aligned} \quad \dots (2)$$

We can now write for the Fourier Transforms of $C_{ii}(r)$ and $C_{ij}(r)$:

$$\rho_{ii} \bar{C}_{ij}(k) = - \frac{24\eta_{ii}}{(k\sigma_{ii})^6} [a_i (k\sigma_{ii})^3 \{\sin k\sigma_{ii} - k\sigma_{ii} \cos k\sigma_{ii}\}]$$

(equation continued on next page)

$$\begin{aligned}
 & + \beta_i (k\sigma_{ii})^2 \{2k\sigma_{ii} \sin k\sigma_{ii} - (k^2\sigma_{ii}^2 - 2) \cos k\sigma_{ii} - 2\} \\
 & + \gamma_i \{(4k^3\sigma_{ii}^3 - 24k\sigma_{ii}) \sin k\sigma_{ii} \\
 & - (k^4\sigma_{ii}^4 - 12k^2\sigma_{ii}^2 + 24) \cos k\sigma_{ii} + 24\} \\
 & + 24\eta_{ii}\epsilon_{ii} (k_B T) \cdot \{(-A_{ii} k\sigma_{ii} \cos A_{ii} k\sigma_{ii} + \\
 & \sin A_{ii} k\sigma_{ii} + k\sigma_{ii} \cos k\sigma_{ii} - \sin k\sigma_{ii}) / (k\sigma_{ii})^3 \} \quad \dots (3)
 \end{aligned}$$

and

$$\begin{aligned}
 \tilde{c}_{12}(k) = & -\frac{4\pi}{k^6} \cdot [\{k^2 (a_1 + 2b\sigma_{11} + 4d\sigma_{11}^2 (\sigma_{12} + 2\lambda) - 24d\sigma_{12}) \\
 & k \sin k\sigma_{12} + \{k^2 (2b + 12d\sigma_{11}\sigma_{22}) \\
 & - k^4 (a_1\sigma_{12} + b\sigma_{11}^3 + d\sigma_{11}^3 (\sigma_{12} + 3\lambda)) - 24d\} \\
 & \cos k\sigma_{12} + (24d - 12bk^2) \cos \lambda k + 24\lambda d k \sin \lambda k\} \\
 & + \frac{4\pi\epsilon_{12}}{k^3 K_B T} \cdot \{-A_{12} k\sigma_{12} \cos A_{12} k\sigma_{12} + \\
 & k\sigma_{12} \cos k\sigma_{12} + \sin A_{12} k\sigma_{12} - \sin k\sigma_{12}\} \quad \dots (4)
 \end{aligned}$$

with $\eta_{ii} = \pi \rho_{ii} \sigma_{ii}^3/6$, $\lambda = (\sigma_{22} - \sigma_{11})/2$, and ρ_{ii} is the number density of the species i . The other constants are as defined by Lebowitz (1964) and Ashcroft and Langreth (1967). Partial structure factors, $S_{ij}(k)$'s are related to $\tilde{C}_{ij}(k)$'s as follows (Ashcroft & Langreth, 1967);—

$$\begin{aligned}
 S_{11}(k) & = [1 - \rho_{11} \tilde{C}_{11}(k) - \rho_{11} \rho_{22} \tilde{C}_{12}^2(k) / \{1 - \rho_{22} \tilde{C}_{22}(k)\}^{-1} \\
 S_{22}(k) & = [1 - \rho_{22} \tilde{C}_{22}(k) - \rho_{11} \rho_{22} \tilde{C}_{12}^2(k) / \{1 - \rho_{22} \tilde{C}_{11}(k)\}^{-1} \\
 S_{12}(k) & = (\rho_{11} \rho_{22})^{1/2} \cdot \tilde{C}_{12}(k) [\{1 - \rho_{11} \tilde{C}_{11}(k)\} \cdot \{1 - \\
 & \rho_{22} \tilde{C}_{22}(k)\} - \rho_{11} \rho_{22} \tilde{C}_{12}(k)]^{-1} \quad \dots (5)
 \end{aligned}$$

In the long wavelength limit, eqns. (3) and (4) reduce to ;

$$\rho_{ii} \tilde{C}_{ii}(0) = -24\eta_{ii} (a_i/3 + b_i \sigma_{ii}/4 + d \sigma_{ii}^3/6) + 8\eta_{ii} \epsilon_{ii} (A_{ii}^3 - 1)/(K_B T)$$

and

$$\begin{aligned}
 \tilde{C}_{12}(0) & = 4\pi \epsilon_{12} \sigma_{12}^3 (A_{12}^3 - 1)/3K_B T - \\
 & 4\pi a_1 \sigma_{12}^3/3 - 4\pi \sigma_{11}^3 \{b (\sigma_{11} + \\
 & 2\sigma_{22})/12 + \lambda d \sigma_{11} (3\sigma_{11} + 5\sigma_{22})/ \\
 & 10 + d\sigma_{11}^3 (2\sigma_{11} + 3\sigma_{22})/30\} \quad \dots (6)
 \end{aligned}$$

Kirkwood and Buff (1951) related compressibility, χ_T of the mixture to $\rho c_{ii}(0)$ and $\tilde{c}_{12}(0)$ as ;

$$\rho \chi_T K_B T = \{1 - C_{11} \rho_{11} \tilde{C}_{11}(0) - C_{22} \rho_{22} \tilde{C}_{22}(0) - 2C_{11} C_{22} \rho_{12} \tilde{C}_{12}(0)\}^{-1} \quad \dots (7)$$

Here C_{11} and C_{22} are atomic fractions of components 1 and 2 respectively.

Recently, Bhatia and Thornton (1970) have introduced three new structure factors. These authors define three correlation functions in terms of fluctuations in (1) the particle density (without regard to type), $S_{NN}(k)$; (2) the composition (i.e., the local concentration as in mole fraction, $S_{CC}(k)$) and (3) the cross-correlation between number and composition, $S_{NC}(k)$. These functions are related to $S_{ii}(k)$ and $S_{ij}(k)$ as ;

$$\begin{aligned} S_{NN}(k) &= C_{11} S_{11}(k) + C_{22} S_{22}(k) + \\ &\quad 2 (C_{11} C_{22})^{1/2} S_{12}(k) \\ S_{CC}(k) &= C_{11} C_{22} [C_{22} S_{11}(k) + C_{11} S_{22}(k) \\ &\quad - (C_{11} C_{22})^{1/2} S_{12}(k)] \end{aligned}$$

and

$$S_{NC}(k) = C_{11} C_{22} [S_{11}(k) - S_{22}(k) + S_{12}(k)(C_{22} - (C_{11} C_{22})^{1/2})] \quad \dots (8)$$

RESULTS AND DISCUSSIONS

Eqns. (3) - (5) have been utilised for the computation of partial structure factors for liquid gold-cobalt alloys with cobalt atomic fraction varying from 0.1 to 0.9 in steps of 0.1. Densities of the components in the alloy were determined from those of the pure components assuming an ideal law of mixing to hold e.g.,

$$\begin{aligned} \rho_{11} &= C_{11} \rho_1^0 \rho_2^0 / \{C_{11}(\rho_2^0 - \rho_1^0) + \rho_1^0\} \\ \rho_{22} &= (1 - C_{11}) \rho_1^0 \rho_2^0 / \{C_{11}(\rho_2^0 - \rho_1^0) + \rho_1^0\} \quad \dots (9) \end{aligned}$$

Here ρ_1^0 and ρ_2^0 are densities of pure components and ρ_{11} and ρ_{22} are those of the components in a mixture having C_{11} as atomic fraction of component 1.

The parameters have been taken from previous works of Rao and Murthy (1975) and Rao and Sen (1976) on pure metals.

Figs. 1-3 show $S_{11}(k)$, $S_{22}(k)$ and $S_{12}(k)$ curves at various concentrations, the concentration being expressed as atom fraction of cobalt. As the atomic fraction of cobalt increases, the peak in $S_{11}(k)$ shifts to the high k side with an increase in height. From eqn. (5), we see that in the limit $\rho_{11} \rightarrow 0$, $S_{11}(k) \rightarrow 1$ and this behaviour is

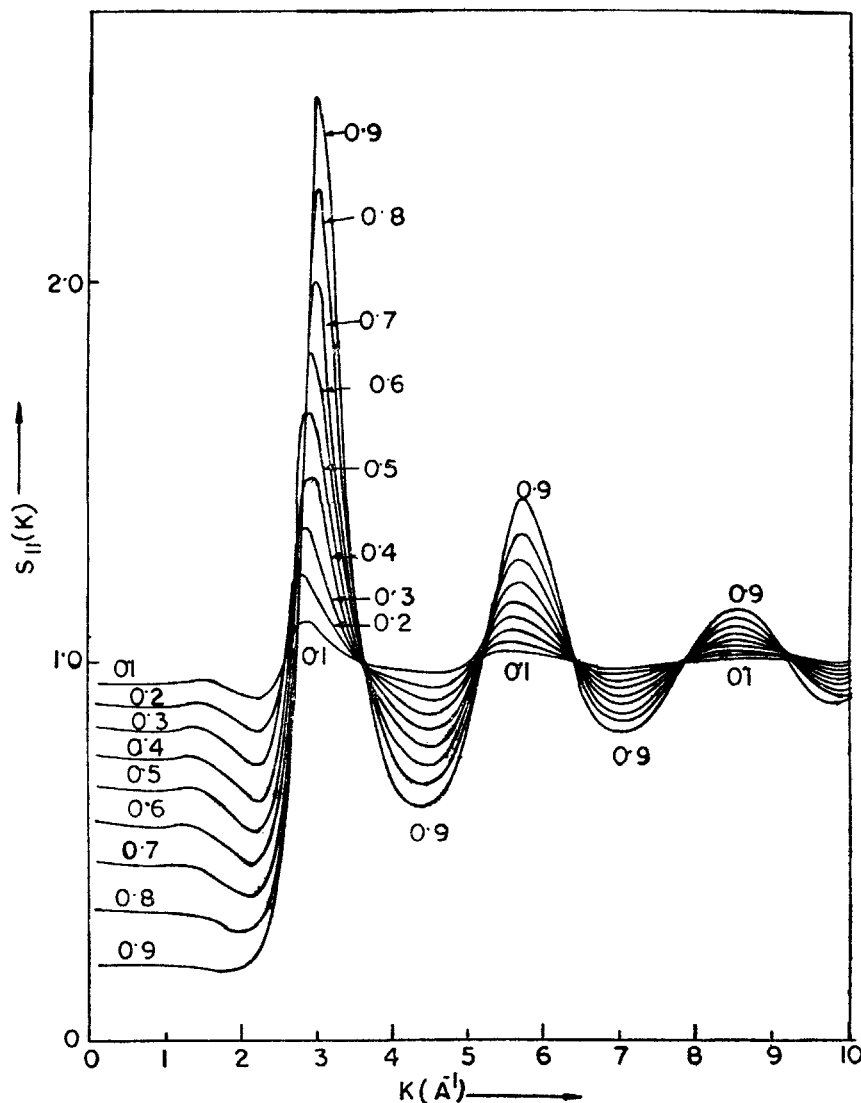


FIG. 1. $S_{11}(k)$ vs. k curves for different atom fractions of cobalt marked against the curves.

seen in Fig. 1. In $S_{22}(k)$ curves, however, peak heights decrease with increase of atom fraction of cobalt while the first peak position shifts to the high k -side (towards the peak position in the pure component case). As $\rho_{22} \rightarrow 0$, $S_{22}(k) \rightarrow 1$ as can be easily verified from eqn. (5). This behaviour is reflected in Fig. 2.

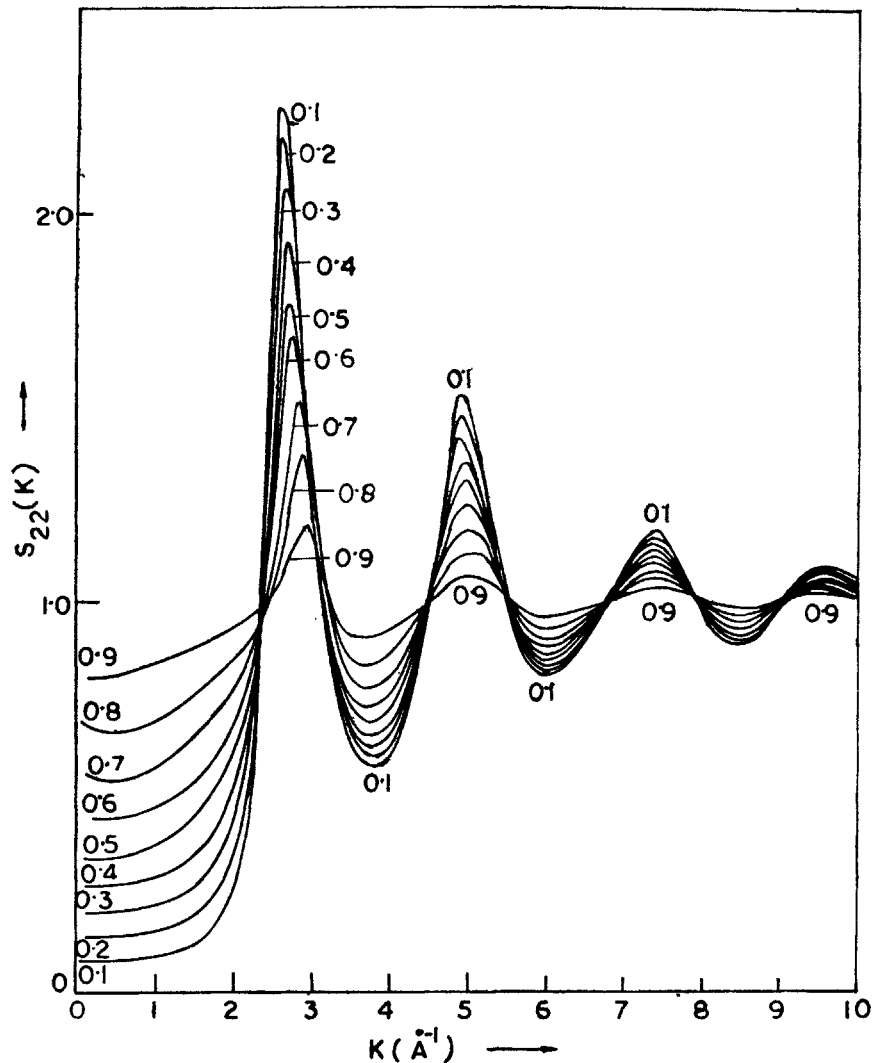


FIG. 2. $S_{22}(k)$ vs. k curves for different atom fractions of cobalt marked against the curves.

$S_{12}(k)$ curves for atom fraction 0.1 to 0.9 of cobalt are shown in Fig. 3. It can be seen that the main peaks in $S_{12}(k)$ curves lie midway between those of $S_{11}(k)$ and $S_{22}(k)$. Here too, the first peak shifts to the high k side while the peak heights increase in the concentration range $0 < C_{11} \leq 0.5$ and then decrease in the concentration range $0.5 < C_{11} < 1.0$. The second and higher peaks show a very slight dependence on the concentration.

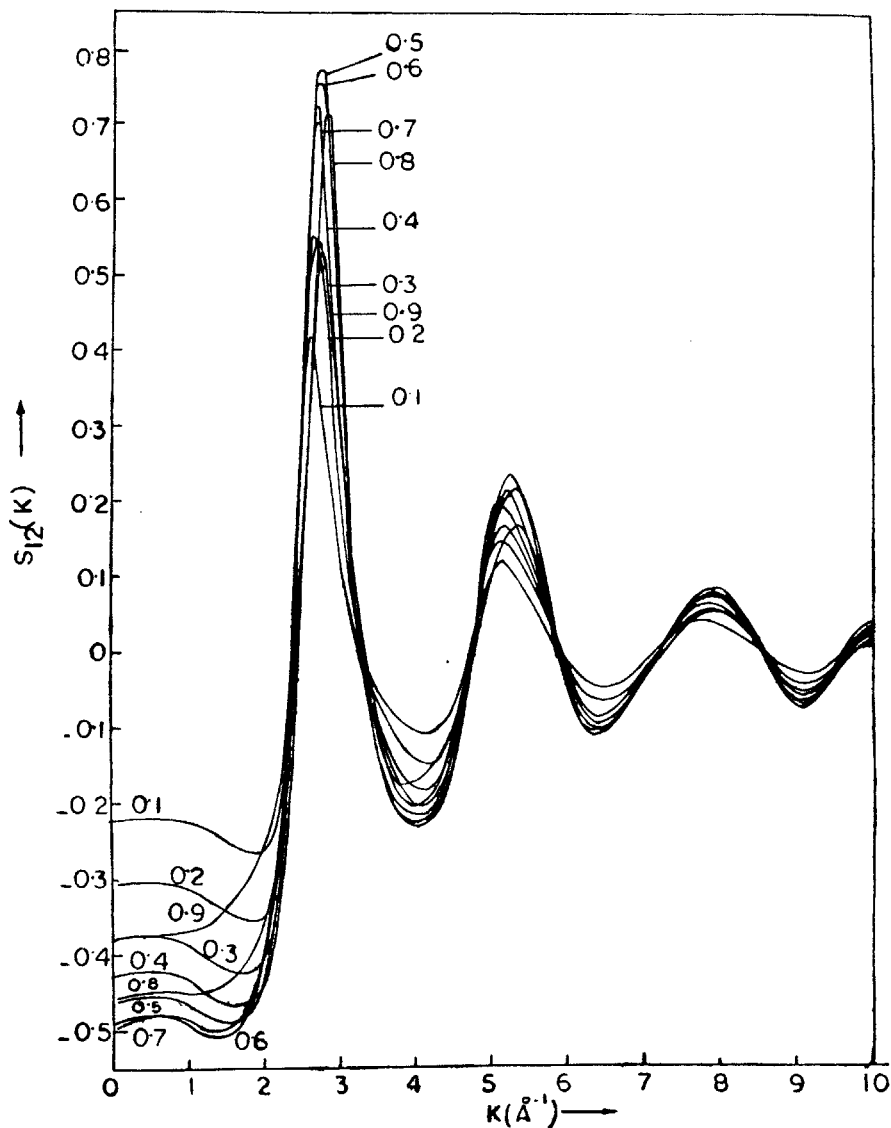


FIG. 3. $S_{12}(k)$ vs. k curves for different atom fractions of cobalt marked against the curves.

Values of $S_{11}(k)$, $S_{22}(k)$ and $S_{12}(k)$ in the long wavelength limit, calculated on the basis of eqns. (5) and (6), are reported in Table I. Values of χ_T , the compressibility of the alloys for various atomic fractions of cobalt are also reported in Table I. Unfortunately, no experimental data are available to compare with our results.

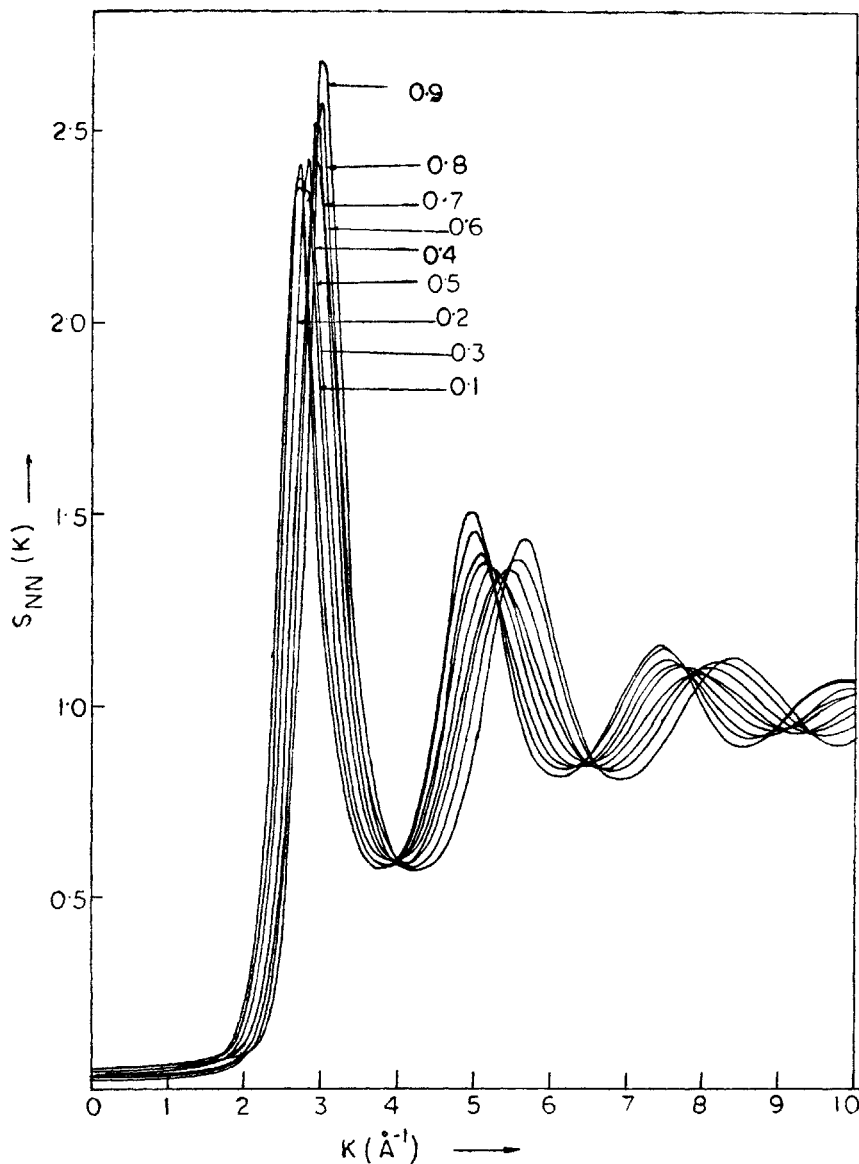


FIG. 4. $S_{NN}(k)$ vs. k curves for different atom fractions of cobalt marked against the curves

$S_{NN}(k)$, $S_{CC}(k)$ and $S_{NC}(k)$ curves for different atom fractions of cobalt are shown in Figs. 4, 5 and 6 respectively. Variation of $S_{NN}(k)$ with k is similar to that of $S(k)$ for a pure liquid. The peak heights in $S_{NN}(k)$ decrease with

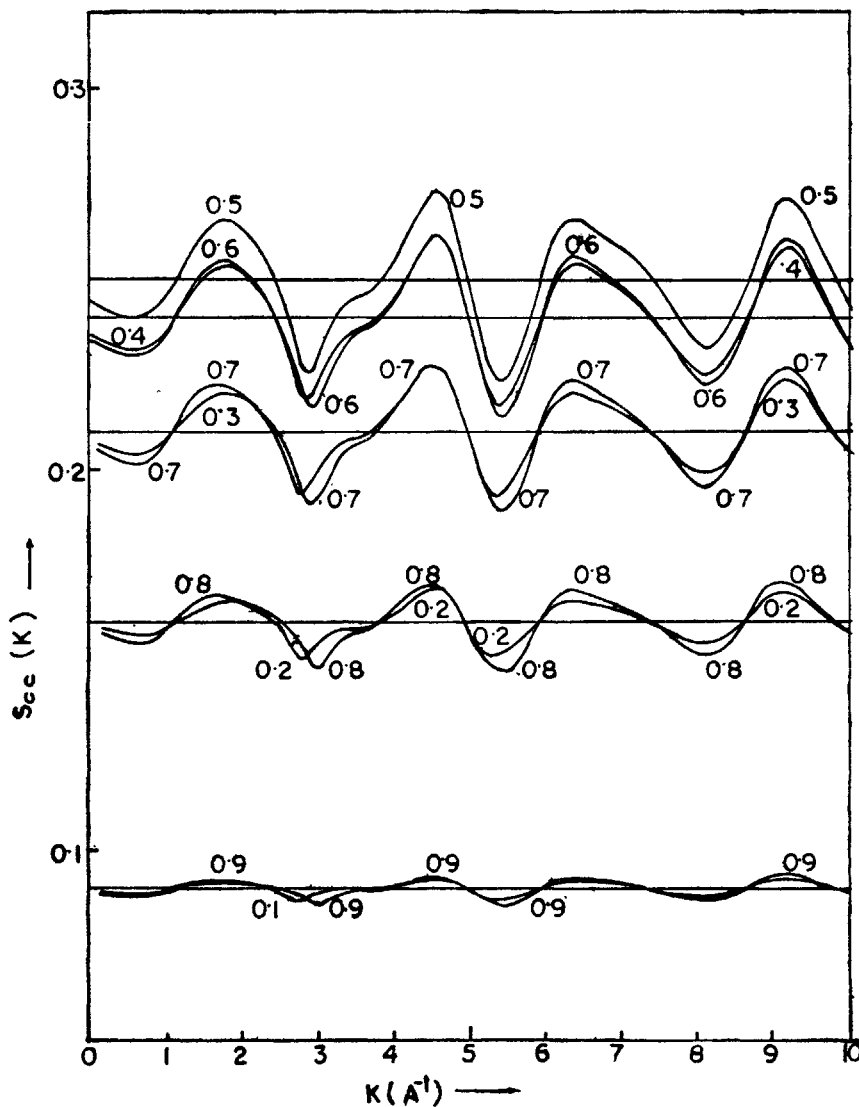


FIG. 5. $S_{CC}(k)$ vs. k curves for different atom fractions of cobalt marked against the curves

increase of atom fraction of cobalt in the range $0 < C_{11} \leq 0.5$ and then increase in the range $0.5 < C_{11} \leq 1$, while the peak position shifts to the low angle side with increase of atom fraction of cobalt. $S_{CC}(k)$ and $S_{NC}(k)$ curves oscillate around $C_{11} \cdot C_{22}$ and 0 respectively. In $S_{NC}(k)$, the peak heights increase with C_{11} in the range $0.5 < C_{11} \leq 1$. This is exactly opposite of the variation of $S_{NN}(k)$ with C_{11} .

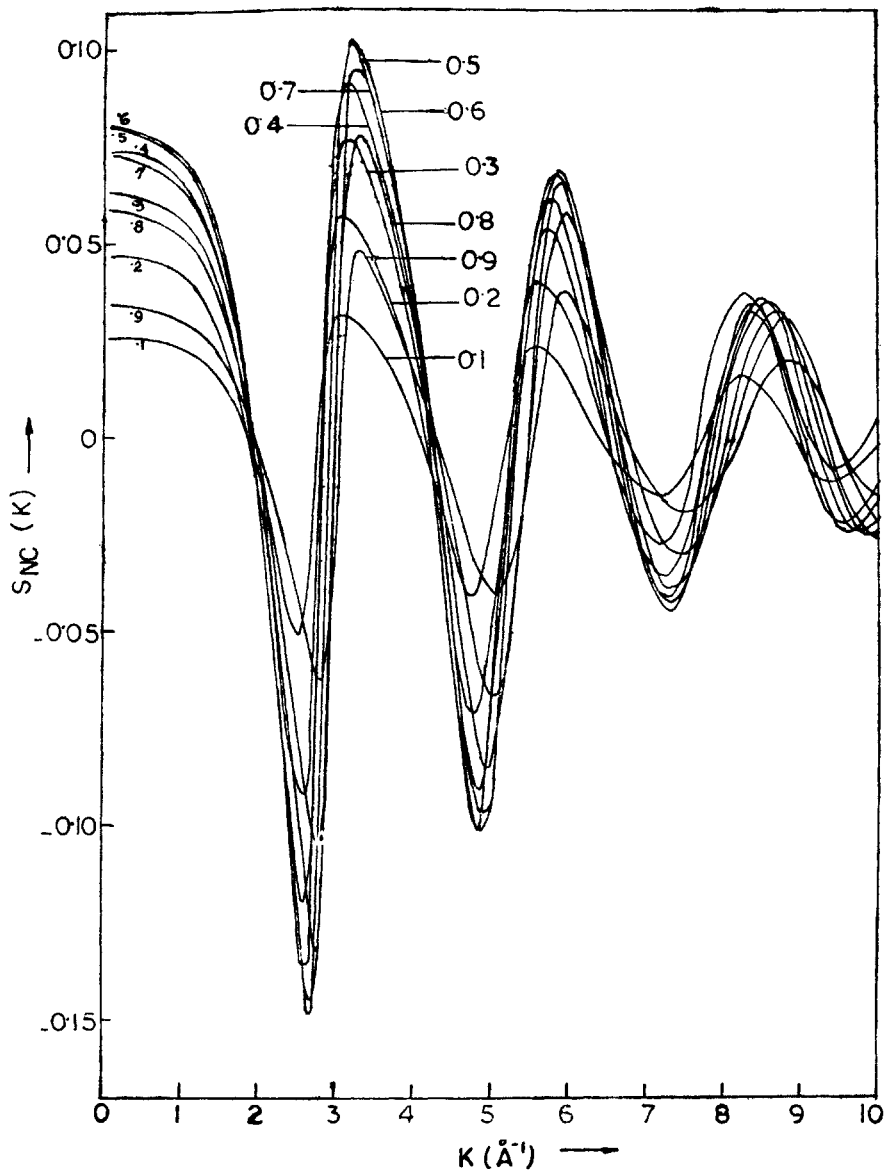


FIG. 6. $S_{NC}(k)$ vs. k curves for different atom fractions of cobalt marked against the curves

Unfortunately, no experimental data are available till date to compare with our results. Nevertheless, this is a very simple way of calculating structural properties of simple alloys and can easily be extended to other simple alloys.

TABLE I

Partial structure factors in the longwave-length limit and isothermal compressibility, χ_T for liquid gold cobalt alloys for different atom fractions of cobalt

Atom fraction of cobalt (C_{11})	S_{11} (0)	S_{22} (0)	S_{12} (0)	$\chi_T \times 10^{12}$ cm ³ dyne ⁻¹
0.1	0.6874	0.0395	-0.1249	1.5960
0.2	0.5111	0.0560	-0.1398	1.5799
0.3	0.3976	0.0704	-0.1430	1.5581
0.4	0.3286	0.0880	-0.1488	1.5298
0.5	0.2592	0.1023	-0.1434	1.4939
0.6	0.2130	0.1247	-0.1447	1.4495
0.7	0.1750	0.1578	-0.1483	1.3956
0.8	0.1412	0.2155	-0.1557	1.3375
0.9	0.1046	0.3473	-0.1683	1.2568

ACKNOWLEDGEMENT

One of the authors (D. Sen) gratefully acknowledges the receipt of a senior fellowship by University Grants Commission (India), during the tenure of which this work has been carried out.

REFERENCES

- Ashcroft, N. W., and Langreth, D. C. (1967). Structure of binary liquid mixtures II. Resistivity of alloys and the ion-ion interaction, *Phys. Rev.*, **159**, 500-510.
- Bhatia, A. B., and Thornton, D. E. (1970). Structural aspects of the electrical resistivity of the binary alloys. *Phys. Rev.*, **2**, B 3004-B 3013.
- Kirkwood, J. G., and Buff, P. (1951). Statistical Mechanical theory of solutions *Indian J. chem. Phys.*, **19**, 774-777.
- Lebowitz, J. L. (1964). Exact solution of generalized Percus-Yevick equation for a mixture of hard spheres. *Phys. Rev.*, **133**, A, 895-A899.
- Rao, R. V. G., and Murthy, A. K. (1975). Structure of liquid noble metals. *Phys. Lett.*, **51**, A, 3-4.
- Rao, R. V. G., and Sen, D. (1976 a). A perturbation treatment of the Percus-Yevick equation and structures of liquid magnesium and cadmium. *Chem. Phys. Lett.*, **43**, 455-456.
- (1976b). Structure factor and isothermal compressibility of liquid transition metals. *Indian J. pure. appl. Phys.*, **14**, 853-855.
- (1977 a). A perturbation treatment of Percus-Yevick equation and structures of liquid Indium and Thallium. *Indian J. Phys.*, **51**, A, 313-316.
- (1976 b). Perturbabtion treatment of Percus-Yevick equation and its application to liquid platinum metals. *Indian J. Phys.*, **51**, A, 382-393.
- Waseda, Y., and Tamaki, S. (1977). On the structure of liquid gold-cobalt alloys. *J. phys., Soc. Japan.*, **43**, 1258-1261.