

Partial structure factors in a liquid or amorphous binary system using anomalous scattering

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Abstract. A method based on the anomalous scattering of either x rays or neutrons has been suggested to separate the partial structure factors in a liquid or amorphous binary system.

1. Introduction

The static structure of a binary system AB, in the liquid or amorphous state is characterized by the three partial structure factors corresponding to the AA, AB and BB pair of atoms. A separation of these individual structure factors is of importance in obtaining information about the nature of interaction between the two types of atoms in the system as well as in the interpretation of their electronic properties. While it is impossible to separate the three partial structure factors from a single scattering experiment, a method based on the combination of data obtained using three different radiations (x rays, neutrons and electrons) or isotopic enrichment (neutron scattering) was suggested by Vineyard (1958) and the relevant expressions were obtained by Keating (1963). The first experimental work using this method is due to Enderby *et al.* (1966) who separated the three partial structure factors in a Cu-Sn system by making measurements of scattered neutron intensity at three different isotope concentrations of copper. The object of this paper is to suggest another method for the separation of the partial structure factors in binary systems where one species of atoms scatters x rays or neutrons anomalously.

Recently from our laboratory, we have investigated the use of anomalous scattering in the determination of the polarization vectors of lattice waves and in the separation of the static displacement due to AA and BB pair of atoms in a binary alloy system (Ramaseshan and Viswanathan 1970, Ramesh and Ramaseshan 1971). In what follows, we shall consider a liquid system although all the arguments equally well apply to an amorphous solid.

2. Anomalous scattering

It is well known that near an absorption edge, the scattering factor for x rays becomes complex leading to many interesting applications in crystallography (see eg Ramaseshan 1963). Peterson and Smith (1961, 1962) showed that some nuclides like ${}^7\text{Li}$, ${}^{10}\text{B}$, ${}^{113}\text{Cd}$, ${}^{149}\text{Sm}$, ${}^{151}\text{Eu}$ and ${}^{157}\text{Gd}$ exhibit resonant elastic scattering of neutrons in the thermal energy region. As in x rays, the scattering length for neutrons becomes complex and can be represented as

$$b = b_0 + b' + ib'' \quad (1)$$

b_0 corresponds to the potential scattering length whereas b' and b'' correspond to the dispersion terms. Figure 1 illustrates the variation with wavelength of these three quantities for ${}^{113}\text{Cd}$ isotope. The salient features of neutron anomalous scattering can be summarized as follows.

(i) Firstly, the dispersion behaviour of b' and b'' is very different from that in x ray anomalous scattering. Secondly, b'' is always positive and exists on either side of the

resonant wavelength whereas in x rays b'' is present only in the short wavelength region of the absorption edge. Further b' can assume both positive and negative values, a behaviour markedly different from that in x rays.

(ii) Secondly, b'/b_0 and b''/b_0 are nearly two orders of magnitude larger as compared with the corresponding quantities for x rays. Typically, b'/b_0 and $b''/b_0 \approx 5-10$ whereas

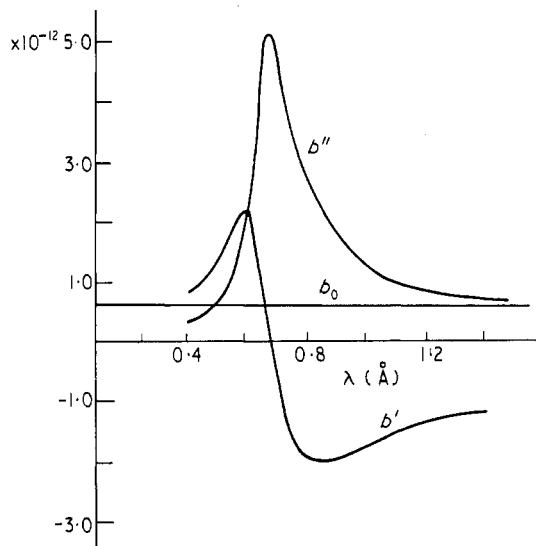


Figure 1. The variation of b' and b'' near the resonant wavelength of ^{113}Cd isotope. The b_0 , b' and b'' are measured in centimetres.

for x rays b'/b_0 and $b''/b_0 \approx 0.1-0.3$. The importance of these large magnitudes of b' and b'' in crystallographic work has been noted by Peterson and Smith (1961, 1962), Ramaseshan (1966) and Singh and Ramaseshan (1968).

3. Liquid structure factor and anomalous scattering

Consider an AB liquid binary system with X_A and X_B representing the atomic fractions of the two species of atoms in the liquid. The x ray notation is used in what follows, but the treatment is valid for neutron scattering also. Let the A species of atoms scatter the radiation anomalously, so that the scattering factor of an A atom could be written as

$$f_A = f_{A_0} + f'_A + if''_A. \quad (2)$$

The intensity of radiation scattered by the system in a direction defined by \mathbf{K} , is given by

$$I_{\text{eu}}(\mathbf{K}) = \left\langle \sum_m \sum_n f_m f_n^* \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle \quad (3)$$

where \mathbf{R}_{mn} represents the interatomic vector connecting the atoms m and n . For a binary system, the expression in (3) can be explicitly written as

$$\begin{aligned} I_{\text{eu}}(\mathbf{K}) = & N \{ X_A f_A f_A^* + X_B f_B f_B^* \} + \left\langle \sum_{m \neq n}^{N_A} \sum_{n \neq m}^{N_A} f_A f_A^* \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle \\ & + \left\langle \sum_{m \neq n}^{N_B} \sum_{n \neq m}^{N_B} f_B f_B^* \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle + \left\langle \sum_{j \neq i}^{N_A} \sum_{i \neq j}^{N_B} f_A f_B^* \exp(i\mathbf{K} \cdot \mathbf{R}_{ij}) \right\rangle \\ & + \left\langle \sum_{m \neq n}^{N_B} \sum_{n \neq m}^{N_A} f_B f_A^* \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle \end{aligned} \quad (4)$$

where $N = N_A + N_B$ is the total number of atoms in the assemblage.

Now

$$\left\langle \sum_{m \neq n}^{N_A N_B} f_A f_B \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle = \left\langle \sum_{m \neq n}^{N_A N_B} (f_{A_0} + f'_A) f_B \cos \mathbf{K} \cdot \mathbf{R}_{mn} \right\rangle - \left\langle \sum_{m \neq n}^{N_A N_B} f''_A f_B \sin \mathbf{K} \cdot \mathbf{R}_{mn} \right\rangle. \quad (5)$$

Assuming that all orientations of \mathbf{R}_{mn} with respect to \mathbf{K} are equally probable in the liquid, we get

$$\overline{\cos \mathbf{K} \cdot \mathbf{R}_{mn}} = \frac{\sin Kr}{Kr} \quad (6a)$$

and

$$\overline{\sin \mathbf{K} \cdot \mathbf{R}_{mn}} = 0 \quad (6b)$$

where $r = |\mathbf{R}_{mn}|$. The second result shows that the sine function, being antisymmetric, averages to zero when \mathbf{R}_{mn} assumes all orientations with equal probability. This is equivalent to the statement that the Patterson function for a centrosymmetric crystal structure is always real, even under the conditions of anomalous scattering. Since the structure of a liquid is statistically centrosymmetric the same result holds good. Making use of the relations (6a) and (6b), the various terms in equation (4) can be expressed in terms of their corresponding pair correlation functions.

$$\begin{aligned} \left\langle \sum_{m \neq n}^{N_A N_A} f_A f_A^* \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle &= \frac{N_A(N_A - 1)}{V} f_A f_A^* \int_0^\infty 4\pi r^2 \{g_{AA}(r) - 1\} \frac{\sin Kr}{Kr} dr \\ &= NX_A^2 f_A f_A^* \int_0^\infty 4\pi r^2 \left\{ \frac{N_A g_{AA}(r)}{V X_A} - \frac{N}{V} \right\} \frac{\sin Kr}{Kr} dr \\ &= NX_A^2 f_A f_A^* \int_0^\infty 4\pi r^2 \left\{ \frac{\rho_{AA}(r)}{X_A} - \rho_0 \right\} \frac{\sin Kr}{Kr} dr \end{aligned} \quad (7)$$

where $\rho_{AA}(r) = (N_A/V) g_{AA}(r)$ represents the atomic density of the A species of atoms at a distance r from an A atom at the origin. The average density of the liquid system is $\rho_0 = N/V$. Introducing the partial structure factor $I_{AA}(K)$ which is defined as

$$I_{AA}(K) = 1 + \int_0^\infty 4\pi r^2 \left\{ \frac{\rho_{AA}(r)}{X_A} - \rho_0 \right\} \frac{\sin Kr}{Kr} dr \quad (8)$$

we get

$$\left\langle \sum_{m \neq n}^{N_A N_A} f_A f_A^* \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle = NX_A^2 f_A f_A^* \{I_{AA}(K) - 1\}. \quad (9)$$

Similarly

$$\left\langle \sum_{m \neq n}^{N_B N_B} f_B f_B \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle = NX_B^2 f_B^2 \{I_{BB}(K) - 1\} \quad (10)$$

where

$$I_{BB}(K) = 1 + \int_0^\infty 4\pi r^2 \left\{ \frac{\rho_{BB}(r)}{X_B} - \rho_0 \right\} \frac{\sin Kr}{Kr} dr. \quad (11)$$

Substituting equation (6b) in equation (5), we get

$$\left\langle \sum_{m \neq n}^{N_A} \sum^{N_B} f_A f_B \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle = N X_A X_B (f_{A_0} + f'_A) f_B \{I_{AB}(K) - 1\} \quad (12)$$

where

$$I_{AB}(K) = 1 + \int_0^\infty 4\pi r^2 \left\{ \frac{\rho_{AB}(r)}{X_B} - \rho_0 \right\} \frac{\sin Kr}{Kr} dr. \quad (13)$$

Since $X_A \rho_{AB}(r) = X_B \rho_{BA}(r)$,

$$\left\langle \sum_{m \neq n}^{N_B} \sum^{N_A} f_B f_A^* \exp(i\mathbf{K} \cdot \mathbf{R}_{mn}) \right\rangle = N X_A X_B (f_{A_0} + f'_A) f_B \{I_{AB}(K) - 1\}. \quad (14)$$

It is to be noted that the partial structure factor $I_{AB}(K)$ in equations (12) and (14) is associated with only $(f_{A_0} + f'_A)$, the real part of the scattering factor of an A atom. Combining the results from equation (9) to equation (14), the expression for the coherent part of the scattered radiation (without the small angle scattering) takes the form

$$\begin{aligned} \frac{I_{cu}(K)}{N} &= X_A f_A f_A^* + X_B f_B^2 + X_A^2 f_A f_A^* \{I_{AA}(K) - 1\} + X_B^2 f_B^2 \{I_{BB}(K) - 1\} \\ &\quad + 2X_A X_B (f_{A_0} + f'_A) f_B \{I_{AB}(K) - 1\}. \end{aligned} \quad (15)$$

It can be clearly seen from equation (15) that when the partial structure factors tend to their asymptotic value of unity, the expression for the intensity reduces to the sum of the contributions from the individual components.

The scattering factor terms f'_A and f''_A are wavelength dependent so that by choosing a different wavelength for the incident radiation, one can effectively change the scattering factor of an A atom. It is clear that a measurement of the intensity of the coherently scattered radiation at two wavelengths near the absorption region of an A atom provides two additional relations of the form given by equation (15). This data when combined with the one obtained from normal scattering leads to a separation of the three partial structure factors $I_{AA}(K)$, $I_{BB}(K)$ and $I_{AB}(K)$.

It may be noted that in neutron scattering, $(f_{A_0} + f'_A)$ can be made negative in the region close to the absorption frequency on the long wavelength side. If in a binary liquid, the interaction between the unlike atoms predominates, then a Fourier inversion of the measured intensity yields the reduced pair correlation function whose first peak has a negative strength. The presence of the unlike atom interaction in a liquid alloy can therefore be detected by a single scattering experiment near the absorption region though a quantitative determination of the pair correlation functions, requires three independent scattering data.

4. Conclusion

It is shown that using anomalous scattering of either x rays or neutrons, one can separate the partial structure factors in a liquid binary system. This method can also be utilized in the analysis of the intensity data from amorphous binary alloys.

Appendix

The intensity expression for the total scattering as given by equation (15) can be written in an alternative form on introducing a different definition for the partial structure factor. The alternative definition of the partial structure factor takes the form

$$I'_{x\beta}(K) = 1 + (X_x X_\beta)^{1/2} \int_0^\infty 4\pi r^2 \left\{ \frac{\rho_{x\beta}(r)}{X_\beta} - \rho_0 \right\} \frac{\sin Kr}{Kr} dr. \quad (16)$$

$I'_{\alpha\beta}(K)$ is related to $I_{\alpha\beta}(K)$ used in equation (15) by the relation,

$$I_{\alpha\beta}(K) = 1 + \frac{I'_{\alpha\beta}(K) - 1}{(X_{\alpha}X_{\beta})^{1/2}}. \quad (17)$$

Making use of equation (17) the intensity expression as given by equation (15) takes the form

$$\begin{aligned} \frac{I_{eu}(K)}{N} = & X_A f_A f_A^* I'_{AA}(K) + X_B f_B^2 I'_{BB}(K) + 2(X_A X_B)^{1/2} (f_{A_0} + f'_A) f_B I'_{AB}(K) \\ & - 2(X_A X_B)^{1/2} (f_{A_0} + f'_A) f_B. \end{aligned}$$

References

- ENDERBY, J. E., NORTH, D. M., and EGELSTAFF, P. A., 1966, *Phil. Mag.*, **14**, 961-70.
 KEATING, D. T., 1963, *J. appl. Phys.*, **34**, 923-5.
 PETERSON, S. W., and SMITH, H. G., 1961, *Phys. Rev. Lett.*, **6**, 7-9.
 ——— 1962, *J. Phys. Soc. Japan*, **17**, 335-9.
 RAMASESHAN, S., 1963, *Advanced Methods in X ray Crystallography* (London: Academic Press).
 ——— 1966, *Current Sci.*, **35**, 87-91.
 RAMASESHAN, S., and VISWANATHAN, K. S., 1970, *Acta Crystallogr.*, **A26**, 364-6.
 RAMESH, T. G., and RAMASESHAN, S., 1971, *Acta Crystallogr. A*, **27**, 332-41.
 SINGH, A. K., and RAMASESHAN, S., 1968, *Acta Crystallogr.*, **B24**, 35-9.
 VINEYARD, G. H., 1958, *Liquid metals and Solidification* (Cleveland, Ohio: American Society for Metals), pp. 1-48.
 WAGNER, C. N. J., and HALDER, N. C., 1967, *Adv. Physics*, **16**, 241-61.