

ANOMALOUS AND RESONANCE SMALL ANGLE SCATTERING*

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FEB 11 1988

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November 1987

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INVITED PAPER submitted to International Conference on Applications and Techniques of Small Angle Scattering, Argonne National Laboratory, Argonne, IL, October 26-29, 1987.

*Work supported by the U. S. Department of Energy, BES-Materials Sciences, under contract W-31-109-ENG-38.

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Abstract

Significant changes in the small angle scattered intensity can be induced by making measurements with radiation close to an absorption edge of an appropriate atomic species contained in the sample. These changes can be related quantitatively to the real and imaginary anomalous dispersion terms for the scattering factor (X-rays) or scattering length (neutrons). The physics inherent in these anomalous dispersion terms is first discussed before considering how they enter the relevant scattering theory. Two major areas of anomalous scattering research have emerged; macromolecules in solution and unmixing of metallic alloys. Research in each area is reviewed, illustrating both the feasibility and potential of these techniques. All the experimental results reported to date have been obtained with X-rays. However, it is pointed out that the formalism is the same for the analogue experiment with neutrons, and a number of suitable isotopes exist which exhibit resonance in an accessible range of energy. Potential applications of resonance small angle neutron scatterings are discussed.

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ANOMALOUS AND RESONANCE SMALL ANGLE SCATTERING

J. E. Epperson and P. Thiyagarajan

I. Introduction

The techniques of small angle X-ray and small angle neutron scattering are closely related. That there are significant differences also is not surprising if one recalls the means by which scattering occurs; in the former case, scattering takes place when X-ray photons interact with electrons in the sample and in the latter case when the neutrons interact with target nuclei via purely nuclear forces or when the magnetic moments of the projectile neutrons interact with the magnetic moments of the target electrons. Conventionally, the physics inherent in this interaction between the projectile X-rays or neutrons and the target atoms is contained in the scattering factor, f , or scattering length, b , respectively, as will be discussed presently.

The bulk of small angle scattering work done to date has employed radiation whose energy is relatively far from that of an atomic absorption edge in the sample. In this classical work, the scattering factor (scattering length) takes on a simple form, independent of the wavelength, λ , being employed. However, it is well known⁽³⁰⁾ that in the immediate vicinity of an absorption edge of a scattering atom, the scattering factor (scattering length) is strongly wavelength dependent. This fact, taken in conjunction with the present availability of intense, wide-band sources, synchrotrons for X-rays and high flux reactors or pulsed sources for neutrons, offers the opportunity for carrying out experiments which can yield information not

readily available from more conventional experiments, e.g., the distribution of the resonant atoms in the sample.

When near-resonance X-rays are utilized, the technique is known as anomalous scattering, and when near-resonance neutrons are employed, the common designation is resonance scattering, although the basic principles are the same. These techniques are complementary to the more widely used isotopic substitution method in neutron small angle scattering, a subset of which is treated elsewhere.⁽⁵³⁾ A fundamental distinction is that in anomalous and resonance scattering techniques, the identical sample is used for all required scattering experiments; in effect, one has perfect isomorphous replacement. This distinction may be crucial when dealing with materials which are sensitive to the details of preparation. Note, however, that one may still need to label a site (or sites) in order to provide a vehicle for anomalous or resonance scattering; once this labeling is done, scattering contrast is varied by merely changing the incident wavelength.

II. Anomalous Dispersion

Before considering applications of anomalous or resonance small angle scattering, it is worthwhile reviewing the wavelength dependence of the scattering factor and scattering length.

a) The X-ray Scattering Factor

The coherent atomic scattering factor for X-rays is conventionally defined as the ratio of the amplitude of a wave scattered coherently by an atom to that scattered by a single classical electron, under the same conditions. The common tabulations of X-ray scattering factors are only first

approximations calculated by self-consistent quantum mechanical methods. (15,31) The fundamental assumption upon which these tabulated values are based is that the electrons in the atoms are so loosely bound that they scatter as free electrons according to the classical Thomson theory. Furthermore, since the electron is to be bound to the nucleus so as to form an atom, one assumes the frequency of the incoming radiation is much greater than that of the natural absorption frequencies and that the orbital motion of the electrons is slow compared to alterations of the field vector of the incoming radiation. In the forward direction, under the stated assumptions, the atomic scattering factor is equal to the number of electrons in the atom; i.e., the atomic number Z . However, because of the finite volume throughout which electronic wave-functions are distributed, interference effects are produced at non-zero scattering angles resulting in the well-known angle dependence of the scattering factor; this variation with angle can usually be ignored in small angle scattering. It should thus be emphasized that these tabulated values of the atomic scattering factors are valid only for wavelengths far from an atomic absorption edge in the sample.

More generally, the atomic scattering factor may be represented as

$$f = f_0 + f' + if'', \quad (1)$$

where f_0 is the high frequency limit discussed in the previous paragraph, and f' and f'' are the real and imaginary components, respectively, of the dispersion correction. All the physics associated with the wavelength dependence is contained in f' and f'' . The real part of the dispersion correction represents in-phase scattering and can be expressed for angular frequency ω as

$$f'(\omega) = \sum_i \int_{\omega'=0}^{\omega} \frac{\omega'^2 (dg/d\omega')_i}{\omega^2 - \omega'^2} d\omega', \quad (2)$$

$$\text{where } \omega = \frac{2\pi c}{\lambda}, \quad (3)$$

c is the velocity of light, and $(dg/d\omega')_i$ is the oscillator density for type i oscillators. The summation extends over all types of electrons in the atom. The complex component represents a phase shift of 90° and can be expressed as

$$f''(\omega) = \frac{\pi\omega}{2} \sum_i (dg/d\omega)_i. \quad (4)$$

The strong wavelength dependence of f' and f'' in the vicinity of an absorption edge is illustrated in Fig. 1 for values of the dispersion correction for Fe calculated by Saravia and Caticha-Ellis⁽⁴⁰⁾ and Cromer.⁽¹⁰⁾ There is an abrupt decrease in f'' as λ increases through the absorption edge and a sharp decrease in f' as the absorption edge is approached from either side, and a singularity at the absorption edge. Clearly, precise knowledge of the dispersion terms is required if scattering experiments in close proximity of an absorption edge are to be successful.

Near a given absorption edge, anomalous dispersion will be dominated by contributions from one type oscillator only, and the summations in Eqs. (2) and (4) may be dropped. The dispersion correction terms are then conveniently linked by the non-relativistic Kronig-Kramers relationship:⁽³²⁾

$$f'(\omega) = \frac{2}{\pi} \oint_{\omega'=0}^{\infty} \frac{\omega' f''(\omega') d\omega'}{\omega^2 - \omega'^2}, \quad (5)$$

where \oint indicates the Cauchy principal value for the integral.

The existence of a complex atomic scattering factor denotes absorption of X-rays by the sample, and optical theory provides a relationship between the linear photoelectric absorption coefficient, μ , and the imaginary component of the dispersion correction:⁽³⁰⁾

$$\mu(\omega) = \frac{4\pi N e^2}{m\omega c} f''(\omega), \quad (6)$$

where m and c are the mass and charge, respectively, of an electron and N is the number of atoms per unit volume of sample. Precise, high resolution absorption measurements, corrected for Compton scattering and thermal diffuse scattering, and use of Eqs. (5) and (6) appear to represent the most straightforward means of determining f'' and f' . Gerward et al.⁽²⁰⁾ have carried out such measurements on Si and Ge and point out that this procedure yields f'' values in good agreement with the relativistic, quantum mechanical calculations by Cromer and Liberman^{(11,12)*}; however, they argue that such a procedure yields only the photoelectric contribution to f' and that a relativistic correction, associated with summation over negative intermediate states, must also be included. When this correction, amounting to $5E_{\text{tot}}/3mc^2$ or -0.026 electrons for Si (E_{tot} is the total energy of an atom), was applied, excellent agreement of their experimental f' values with the Cromer-Liberman calculations was observed. These authors point out that for high energies and/or for high atomic numbers yet another frequency dependent, magnetic term must be included. Their conclusion was that in order to determine experimentally, and directly, the real dispersion correction

*The classical calculations by Hönig^(23,24) were carried out only for the K electrons using hydrogenic wavefunctions.

appropriate for a diffraction experiment, one needs to measure the refractive index of the material or use a direct scattering experiment.

Hoyt, de Fontaine, and Warburton⁽²⁸⁾ have reviewed practical considerations, including the effect of various systematic errors, of carrying out such a determination from absorption measurements. In particular, it should be noted from Eq. (5) that absorption measurements over a wide range of energies are required in order to determine f' accurately. They point out the inability of even the most rigorous, present-day f' and f'' calculations to predict near-edge effects. From an extensive series of EXAFS measurements at a synchrotron source, they evaluated both f'' and f' (corrected as discussed above) for Cu, Ni, and Ti near the K absorption edges, and their results for Ni are shown in Fig. 2. These results dramatize even more the need for experimental values of the dispersion correction when working close to an absorption edge.

Although the absorption method just outlined appears, in many respects, to be the most straightforward means of determining experimentally the dispersion correction terms, several other techniques have been employed. Among the other methods that have been utilized are, for example, interferometry⁽³⁾ total reflection,⁽¹⁷⁾ index of refraction by the prism method,⁽¹⁴⁾ and integrated intensity measurements.^(16,48)

It has long been recognized that anomalous scattering effects may be larger at L edges than at K edges.^(6,8) This fact is significant inasmuch as one is usually seeking enhanced contrast in an anomalous scattering experiment. Templeton and Templeton⁽⁴⁸⁾ have measured the integrated intensities of some 40 Bragg reflections from single crystals of cesium hydrogen (+)-tartrate with synchrotron radiation at 52 wavelengths spanning the three L absorption edges of Cs. The non-centrosymmetric structure meant

that Bijvoet pairs were available which aided in the determination of f'' . The structural parameters for this material were known accurately from previous conventional work^(49,50) at another off-resonance wavelength, enabling them to utilize least squares refinement procedures to derive the f' and f'' values for cesium. Near the L_3 edge, f' was found to vary between -26.7 and -13.9 and f'' between 4.0 and 16.1 electrons in a wavelength interval of only 0.008 Å. Their experimental values for f' and f'' near the L_3 edge of Cs are shown in Fig. 3, along with the corresponding calculated values by Cromer. Lack of fine detail in the calculations is attributed to the fact that the model neglects modulations of density of states in the continuum and transitions to vacant bound states.

b. The Neutron Scattering Length

Conventional coherent neutron scattering arises from the nuclear interaction between the projectile neutron and the nucleus of the target atom. In addition, if an atom has unpaired electrons, it may scatter neutrons because of a dipole interaction between the resulting magnetic moment of the atom and that of the neutron. In the discussion to follow, we shall deal exclusively with nuclear scattering.

One component of nuclear scattering is measured by the effective geometric cross section the nucleus presents to the incoming neutron. This is the potential scattering and is found to increase proportional to the cube root of the atomic mass of the nucleus. A process known as resonance scattering is superimposed on the potential scattering. It is convenient to think of the incident neutron and target atom as momentarily forming a compound nucleus, and, depending on the nature and positions of the energy levels of this compound state, scattering or absorption of the neutron may

result. The amplitude of the resonance scattering may be of the same or opposite sign as that of the potential scattering; in some cases the resulting total coherent scattering amplitude is negative. Resonance scattering varies in a non-regular manner with atomic number, and can even be quite different for different isotopes of a given type atom.

The neutron incident on the nucleus can be represented⁽²⁾ by a plane wave

$$\psi = e^{ikz} \quad (7)$$

where $k = 2\pi/\lambda$ is the wave number and z is a real space position variable. The scattered neutron wave will be spherically symmetrical and can be expressed as

$$\psi_s = -(b/r)e^{ikr}, \quad (8)$$

where r is the radial distance from the nucleus to the point of observation. The quantity b is defined as the scattering length and, in analogy with Eq. (1) for X-rays, can be written in complex notation as

$$b = b_0 + b' + ib'' . \quad (9)$$

The term b_0 corresponds to the high frequency limit, and b' and b'' are the real and imaginary dispersion terms associated with resonance. Because the nuclear dimension is small compared to the wavelength of the incoming neutron, b is independent of the scattering angle.

In the parlance of neutron scattering, it is more common to talk about the elastic scattering cross section which is defined as

$$\sigma = 4\pi b^2. \quad (10)$$

On the assumption that a single resonance energy level is operational, Breit and Wigner⁽⁵⁾ gave an expression for the scattering cross sections:

$$\sigma = 4\pi \left| R + \frac{1/2\Gamma_n/k}{(E-E_r) + 1/2i\Gamma} \right|^2, \quad (11)$$

where R is the nuclear radius, E is the energy of the incident neutron, E_r is the energy the neutron must have to produce resonance in the compound nucleus and $\Gamma = \Gamma_n + \Gamma_a$. Γ_n and Γ_a are the widths of the resonance for re-emission of the neutron with its original energy and for absorption, respectively. The two terms in Eq. (11) correspond to potential and resonance scattering, respectively. Both Γ_n and Γ_a are positive, but note that $(E-E_r)$ may be either positive or negative. After some algebraic manipulation, one can write the Breit-Wigner expression for the neutron scattering length as

$$b = [R] + \left[\frac{1/2 (E-E_r) \Gamma_n/k}{(E-E_r)^2 + 1/4 \Gamma^2} \right] - \left[\frac{1/4 \Gamma \Gamma_n/k}{(E-E_r)^2 + 1/4 \Gamma^2} \right] i \quad (12)$$

or, equivalently, the modulus of the scattering cross section is

$$\sigma = 4\pi \left\{ \left[R + \frac{1/2(E - E_r)\Gamma_n/k}{(E-E_r)^2 + 1/4 \Gamma^2} \right]^2 + 1/16 \left[\frac{\Gamma \Gamma_n/k}{(E-E_r)^2 + 1/4 \Gamma^2} \right]^2 \right\}. \quad (13)$$

For high neutron energies, the cross section approaches $4\pi R^2$; i.e., the scattering length approaches the nuclear radius.

At low energies, the scattering length approaches $R - \frac{1/2 \Gamma_n / k}{E_r}$; that is, it is less than R by a constant amount which depends through Γ_n on the details of the nuclear resonance. A few isotopes exist for which resonance occurs in an energy range accessible at current thermal and near-thermal sources, and it is instructive to consider the wavelength dependence of the scattering length near resonance. The resonance parameters E_r , Γ_n , Γ_a , and R can be evaluated from measurements of the absorption and scattering cross sections as a function of neutron energy. For example, Brockhouse⁽⁷⁾ found for ^{113}Cd that $E_r = 0.178$ eV ($\lambda_r = 0.68$ Å), $\Gamma_a = 0.113$ eV, $\Gamma_n = 0.00068$ eV and $R = 0.70 \times 10^{-12}$ cm; and Marshak et al.⁽³⁷⁾ found for ^{149}Sm that $E_r = 0.0976$ eV ($\lambda_r = 0.92$ Å), $\Gamma_a = 0.0635$ eV, $\Gamma_n = 0.00047$ eV and $R = 0.70 \times 10^{-12}$ cm. The various components of the scattering lengths for ^{113}Cd and ^{149}Sm are shown in Fig. 4. Notice b' vanishes at the resonance wavelength and changes from positive to negative values as λ increases through the resonance point. On the other hand, b'' never goes negative and reaches its maximum value at the resonance wavelength.

The foregoing discussion is strictly valid only for spin zero isotopes. In general, if the nucleus has spin I , the incident neutron and the resonant isotope can combine to form spin states of $I + 1/2$ and $I - 1/2$, but only one of these states will show resonance. For a resonant nuclei with spin I , the probability for compound nucleus formation is $(I + 1)/(2I + 1)$ and the statistical factors for ^{113}Cd ($I = 1/2$) and ^{149}Sm ($I = 7/2$) are 0.75 and 0.56, respectively. This spin factor is included in Fig. 4a and 4b.

The discussion so far clearly illustrates the similarities in the anomalous X-ray and resonance neutron scattering cross sections. However, it is worthwhile noting some important differences in these phenomena. In the case of X-rays, almost all the heavier elements could serve as useful

anomalous scatterers (either K or L edges). But the magnitudes of the $\Delta f'$, $|f_0 - f'|$, values could vary only by about 20 percent of the f_0 values. In the case of neutrons, Bacon⁽²⁾ lists the four isotopes in Table I as being available for resonance scattering in the thermal range; in fact, there are a few other isotopes available for this use also. In contrast to the X-ray case, however, the magnitudes of the $\Delta b'$, $|b_0 - b'|$, values could vary by as much as about seven times that of the b_0 values. In addition, the details of the dispersion behavior of b' and b'' near the resonance point are different from their respective counterparts of anomalous X-ray scattering as shown in Figs. 1 and 4.

Table I. Scattering Amplitudes for Resonant Nuclei

Element or		Resonant $\lambda(\text{\AA})$	b'' (10^{-12} cm)	
Isotope	Abundance		At resonance	At $\lambda = 1 \text{\AA}$
Cd		0.68	0.58	0.15
¹¹³ Cd	0.12	0.68	4.70	1.2
Sm		0.92	0.88	0.7
¹⁴⁹ Sm	0.14	0.92	6.30	5.1
Eu		0.6	1.31	0.07
¹⁵¹ Eu	0.48	0.6	2.74	0.15
Gd		1.8	1.2	0.8
¹⁵⁷ Gd	0.16	1.8	6.60	

III. Theoretical Considerations

Insight into the importance of the anomalous dispersion terms on the resulting small angle scattering can be obtained by considering the complex scattering factor in the formal expression for the scattered intensity. This will also allow an assessment of the accessibility of the structural information contained in the anomalous scattering data. Because the published experimental work to date has been exclusively with X-rays, the following discussion will deal with anomalous scattering of X-rays. However, it follows directly from the preceding section that the formalism would be the same for neutrons if one replaced the scattering factor (f) with the scattering length (b), keeping in mind that the mechanism of scattering is different in the two cases.

The amplitude of the scattered wave from the scattering entity can be written as

$$A = \sum_i f_i e^{2\pi i \vec{k} \cdot \vec{r}_i}, \quad (14)$$

where the summation extends over all atoms in the scattering entity. The intensity is given by the amplitude times its complex conjugate and can be expressed generally as

$$I(q) = \sum_i \sum_j [(f_o + f')_i (f_o + f')_j + f_i'' f_j''] \cos q r_{ij} \\ + \sum_i \sum_j [(f_o + f')_i f_j'' - f_i'' (f_o + f')_j] \sin q r_{ij}, \quad (15)$$

where $q = 2\pi k$. If the scattering entities take on all possible orientations, e.g., molecules in solution or precipitate particles in a randomly oriented polycrystalline material, the sine term drops out, and

$$\frac{1}{\cos q r_{ij}} = \frac{\sin q r_{ij}}{q r_{ij}}, \quad (16)$$

$$\begin{aligned} \text{hence, } I(q) = & \sum_i \sum_j f_{oi} f_{oj} \frac{\sin^{qr_{ij}}}{q r_{ij}} + \sum_i \sum_j f_i' f_j' \frac{\sin^{qr_{ij}}}{q r_{ij}} \\ & + \sum_i \sum_j f_i'' f_j'' \frac{\sin^{qr_{ij}}}{qr_{ij}} + 2 \sum_i \sum_j f_{oi} f_j' \frac{\sin^{qr_{ij}}}{qr_{ij}}. \end{aligned} \quad (17)$$

These Debye-type expressions⁽¹³⁾ represent, respectively, the contributions from off-resonance scattering, the real anomalous scattering, the complex anomalous scattering, and a cross term contribution.

If three centers of scattering are defined such that

$$\sum_i f_i r_{i\alpha}' = 0 \quad (18a)$$

$$\sum_i f_i' r_{i\beta}' = 0, \quad (18b)$$

$$\text{and } \sum_i f_i'' r_{i\gamma}' = 0, \quad (18c)$$

three corresponding radii of gyration can be defined as follows:

$$R_g^2 = \frac{\sum_i f_i r_{i\alpha'}^2}{\sum_i f_i} = \frac{\sum_i f_i r_{i\alpha'}^2}{N} \quad (19a)$$

$$(R_g')^2 = \frac{\sum_i f_i' r_{i\beta'}^2}{\sum_i f_i'} = \frac{\sum_i f_i' r_{i\beta'}^2}{N'} \quad (19b)$$

$$\text{and } (R_g'')^2 = \frac{\sum_i f_i'' r_{i\gamma'}^2}{\sum_i f_i''} = \frac{\sum_i f_i'' r_{i\gamma'}^2}{N''} \quad (19c)$$

In this notation, point α' represents the non-resonant center of scattering and points β' and γ' the real and imaginary centers of scattering, respectively. Expanding the functions $\frac{\sin x}{x}$ as Taylor series and invoking the parallel axis theorem, Borso⁽⁴⁾ has shown that the scattered intensity can be represented as

$$\begin{aligned} I(q) \cong & N^2 \left(1 - \frac{q^2 R_g^2}{3} + \dots \right) + (N')^2 \left(1 - \frac{q^2 (R_g')^2}{3} + \dots \right) \\ & + (N'')^2 \left(1 - \frac{q^2 (R_g'')^2}{3} + \dots \right) + 2NN' \left(1 - \frac{q^2}{6} [R_g^2 + (R_g')^2 + d^2] + \dots \right), \end{aligned} \quad (20)$$

where d is the distance between points α' and β' . By algebraic rearrangement, this can be written as

$$I(q) = (N+N') \left[1 - \frac{q^2}{3} \left(\frac{N}{N+N'} \right) R_g^2 + \left(\frac{N'}{N+N'} \right) (R_g')^2 + \frac{N N'}{(N+N')^2} \right] + (N'')^2 \left(1 - \frac{q^2 (R_g'')^2}{3} \right) . \quad (21)$$

For cases when $N'' \ll N+N'$, this expression reduces to the more familiar Gaussian form

$$I(q) = N_T^2 \left(1 - \frac{q^2 R_T^2}{3} + \dots \right) \approx N_T^2 e^{-\frac{q^2 R_T^2}{3}} , \quad (22)$$

$$\text{where } N_T = N + N' \quad (23)$$

$$\text{and } R_T^2 = \left(\frac{N}{N+N'} \right) R_g^2 + \left(\frac{N'}{N+N'} \right)^2 (R_g')^2 + \frac{N N'}{(N+N')^2} d^2 . \quad (24)$$

From inspection of these last three equations, it can be seen that N and R_g are obtainable from the extrapolated zero angle scattering and slope, respectively, of a Guinier plot⁽²²⁾ determined with radiation far from resonance. Similarly, N_T and R_g' are obtained from the anomalous scattering measurements made with radiation near the absorption edge. Having determined these parameters, Eq. (24) allows one to solve for d , the distance in the scattering entity between the non-resonant and real dispersive centers of gravity.

IV. Experimental Approaches and Results

As we have seen in section IIa, anomalous small angle X-ray scattering can only be observed for wavelengths in close proximity of an absorption edge. This requirement has the practical consequence of dictating that anomalous small angle X-ray scattering experiments be done at a synchrotron

source where the wavelength is precisely and continuously tunable over a wide range of values and where the flux is high for any wavelength selected.*

(a) Macromolecules in Solution

A useful review of anomalous small angle scattering, largely as applied to macromolecules in solution, has been given by Stuhrmann.⁽⁴⁶⁾ Several existing small angle scattering methods can be used or modified for anomalous or resonance scattering experiments. A method developed by Hoppe⁽²⁵⁾ involves labeling two sites in a molecule with anomalously scattering atoms. The difference spectrum can be formed;

$$\Delta I = I_{12}^a + I_{12}^c - I_1^a - I_2^a, \quad (25)$$

where the subscripts denote which, if any, sites are labeled and the superscripts c and a denote conventional and anomalous scattering experiments, respectively. By use of the procedures outlined in section III, it can be shown that this difference spectrum reduces to

$$\Delta I = 2 (f_1' f_2' + f_1'' f_2'') \frac{\sin q r_{12}}{q r_{12}}. \quad (26)$$

The distance between labeled sites (r_{12}) can then be obtained by determining the zero crossover point.

A procedure proposed by Buldt⁽⁹⁾ can yield certain structural information. This procedure involves inserting a small label of enhanced

*In addition to the customary bending magnet radiation, wigglers and undulators⁽⁴¹⁾ provide the experimentalist with powerful tools for tailoring the beam for special needs.

scattering power into a molecule, and one determines the distance distribution function between this labeled subunit and each other segment in the macromolecule. For this labeled particle, three terms arise in the scattering function:

$$I(q) = I_p(q) + I_{PL}(q) + I_L(q) , \quad (27)$$

where $I_p(q)$ represents interferences within the unlabeled particle, $I_{PL}(q)$ represents interferences between the small bound label and the remainder of the molecule and $I_L(q)$ is the contribution from the unbound label. Here, we are interested in the middle interference term which can be written as

$$I_{PL}(q) = 2 f_L \sum_i f_i \frac{\sin q r_{Li}}{q r_{Li}} . \quad (28)$$

The distribution of distances between the label and every position in the structure is given by the Fourier transform

$$D_{PL}(r) = \frac{2}{\pi} r^2 \int_0^\infty I_{PL}(q) \frac{\sin qr}{q r} q^2 dq . \quad (29)$$

The enhanced clarity in this distribution function relative to that obtained from a Fourier transform of the total coherent scattering function is worth emphasizing. Here, all distances are relative to one point, that of the label, whereas the conventional distribution mentioned would give a convolution of distances of all points with respect to all other points in the molecule.

Motivated by the fact that calcium is an important biological regulator and the obvious interest in its location in a protein, Miake-Lye, Doniach and

Hodgson (38) replaced two Cd^{2+} ions with Tb^{3+} ions in the small protein parvalbumin and utilized three synchrotron X-ray wavelengths in the vicinity of the L_3 edge of the terbium label in such an anomalous scattering investigation. Extrapolated to zero scattering angle, the protein-terbium term is 20% of the protein-protein term and the terbium-terbium term is only 1% under off-resonance conditions. The anomalous scattering produced a 5-7% change in the total scattering due to the protein-terbium term and 0.5% for the terbium-terbium. Approximating the electron density distribution in the protein molecule as a Gaussian function, they least squares fitted the small angle scattering data over the range $0.126 < q < 0.283 \text{ \AA}^{-1}$ in order to estimate R_1 and R_2 , the distances of the two terbium ions from the center of mass of the molecules. They found R_1 and R_2 to be identical, within experimental error, and equal to 13.2 \AA . Their experimental data on parvalbumin is compared in Fig. 5 with a curve calculated from the crystallographic coordinates of the very similar carp parvalbumin. Due to the low signal-noise ratio mentioned above for the terbium-terbium term and the difficulties in correcting for photoelectric absorption and fluorescence, both quite significant factors in anomalous scattering experiments, they were unable to extract the terbium-terbium distance.

Vainshtein, Feigin, Lvov, Gvozdev, Marakushev, and Likhtenshtein⁽⁵²⁾ used groups of four mercury atoms to label hemoglobin molecules. Neglecting the cross term in Eq. (27), they reported a distance of $38 \pm 2 \text{ \AA}$ as the distance between the markers associated with the amino acid residues 93 (cysteine) of the two β -chains of hemoglobin.

Stuhrmann,⁽⁴⁴⁾ Ibel and Stuhrmann,⁽²⁹⁾ Luzzati, Tardieu and Mateu,⁽³³⁾ and Stuhrmann⁽⁴⁵⁾ have devised a different method for obtaining distance

information between labeled subunits. The radius of gyration can, in the notation of Stuhrmann,⁽⁴⁶⁾ be expressed as

$$R^2 = R_c^2 + \alpha \frac{\bar{\rho} + \bar{\rho}'}{(\bar{\rho} + \bar{\rho}')^2 + (\bar{\rho}'')^2} - \frac{\beta}{(\bar{\rho} + \bar{\rho}')^2 + (\bar{\rho}'')^2}, \quad (30)$$

$$\text{where } \alpha = \frac{\int \rho_s(\vec{r}) r^2 dr}{V_c}, \quad (31)$$

$$\beta = \frac{\iint \rho_s(\vec{r}) \rho_s(\vec{r}') \vec{r} \cdot \vec{r}' d^3r d^3r'}{V_c^2}, \quad (32)$$

$$V_c = \int \rho_c(\vec{r}) d^3r = \int \rho(\vec{r}) d^3r \quad (33)$$

and R_c , the non-resonant radius of gyration, is given by

$$R_c^2 = \frac{\int \rho_c(\vec{r}) r^2 dr}{V_c}. \quad (34)$$

In the above expressions $\rho(\vec{r})$ is defined as the excess scattering length density of the particles relative to the solvent

$$\rho(\vec{r}) = \rho(\vec{r})_{\text{solute}} - \rho_{\text{solvent}}, \quad (35)$$

and $\bar{\rho}$ is the overall mean scattering length density with $\bar{\rho}'$ and $\bar{\rho}''$ the mean real and complex anomalous scattering densities, respectively; $\rho_s(\vec{r})$ is the internal structure observed at vanishing contrast and $\rho_c(\vec{r})$ the shape of the molecular volume excluded to the solvent. A change in the apparent radius of gyration with the contrast exists even if there are no anomalous scattering atoms present.

Stuhrmann⁽⁴⁵⁾ has measured the anomalous small angle scattering from iron-storing ferritin at a synchrotron with ten X-ray wavelengths in the vicinity of the K absorption edge of iron and found a systematic 4% variation in the apparent radius of gyration as shown in Fig. 6. Practically no variation in the radius of gyration was found except very near the absorption edge. It was shown that the variation in R illustrated in Fig. 6 could be attributed primarily to changes in f' with wavelength. It was estimated that the presence of Fe in the ferritin, some 3000 atoms per ferritin molecule, resulted in a 14% decrease in contrast for the iron-bearing ferritin.

In a powerful demonstration of the potential of anomalous small angle scattering, Stuhrmann and Notbaum⁽⁴⁷⁾ carried out measurements on hemoglobin at some 32 wavelengths near the K absorption edge of iron at a synchrotron source. Because each hemoglobin molecule contained only four Fe atoms, relative intensity changes of only 0.001 to 0.01 were expected due to anomalous scattering. Absorption effects, which are quite sensitive to the chemical environment^(38,47) along with fluorescence tend to dominate the scattering pattern, and these effects must be carefully corrected for. The anomalous scattering for this system is due to the convolution of the whole molecule with the particular geometrical arrangement of the four iron atoms in the hemoglobin molecule, and this manifests itself in a cross term, the second term on the right of Eq. (27). The anomalous scattering contribution from the Fe alone [third term of Eq. (27)] was too weak to discriminate from the background. Consequently, information about the location of the Fe atoms could only be extracted from consideration of the iron-hemoglobin term. Fortunately, the information about the geometrical arrangement of the anomalous scatterers is obtained relative to the coordinates of the non-resonant structure. A careful multipole analysis of the Fe-hemoglobin cross

ture, with due consideration of what was already known about the chemistry of hemoglobin, suggested a nearly tetrahedral packing of the four subunits of hemoglobin with a radial distance of each Fe atom from the center of mass of the molecule of about 16 Å. Furthermore, their multipole analysis allowed them to conclude that the distance between the tetrahedrally dispersed Fe atoms was 26 ± 4 Å.

b) Metallurgical Alloys

A second major class of anomalous small angle scattering investigations is now emerging, that of composition changes and phase separation in metallic alloys. A useful review of the merits of the anomalous scattering and isotopic substitution methods for this application has been given by Simon, Lyon, and de Fontaine.⁽⁴³⁾ In particular, the scattering from a phase separating ternary alloy was simulated, and the effect on the solution in terms of the partial structure functions due to several possible experimental errors was investigated. They observed, "It appears that neutron scattering, although having good contrast, is not suited to these studies since slight structural differences between the three samples may lead to erroneous results." Of course, this observation is not operational if resonance small angle scattering can be employed; then the experiment becomes the exact analogue of anomalous X-ray scattering which allows one to use a single sample for all wavelengths. Precautions and corrections required in such an investigation have been discussed with respect to a preliminary experiment on an Al-Zn alloy by Goudeau, Fontaine, Naudon, and Williams.⁽²¹⁾

For a ternary alloy, the scattered intensity can be expressed as a linear combination of the partial structure functions:

$$I(q) = \sum_{i,j=1}^2 (f_i - f_m) (f_j - f_m)^* S_{ij}(q), \quad (36)$$

where f_m is the scattering factor of the major constituent and f_i and f_j those of the two solutes. S_{ij} is the partial structure function; that is, the Fourier transform of the pair correlation function for components i and j . The basic strategy for determining the partial structure functions is to carry out the experimental measurements with three distinctly different values of the scattering factors. Salva-Ghilarducci, Simon, Guyot and Ansara⁽³⁹⁾ approached this for the Al-Zn-Ag system with small angle neutron scattering by using different, isotopically enriched alloys.* Metallic alloys, usually being non-equilibrium structures, are notorious for difficulties in reproducing exactly the microstructure for different samples of the same alloy, as indicated by the observation cited above. Lyon and co-workers⁽²⁴⁾ have studied the composition changes during unmixing in the ternary Al-Zn-Ag system by means of anomalous small angle X-ray scattering, in the vicinity of the K absorption edge of Zn. They conclude³ that experiments at a single edge were insufficient to extract the desired partial structure functions because of relatively small variations in contrast; only weighted sums could be obtained. They resorted to a lower order approximation; i.e., that the ternary alloy could be treated as a quasi-binary alloy consisting of precipitates of fixed composition growing in a matrix depleted in solute. This procedure allowed a determination of the directions of the tie lines in the Gibbs triangle as shown in Fig. 7.

*In an earlier effort to characterize the metastable equilibrium in ternary Al-Zn-Mg alloys, Gerold, Epperson, and Kostorz⁽¹⁹⁾ used both X-rays and neutrons as a means of varying the scattering power.

The boundaries of the metastable miscibility gap could not be determined, however, because of insufficient beam flux to measure the integrated intensity. From the small angle scattered integrated intensity one can determine the invariant

$$Q_o = 4\pi \int I(q) q^2 dq , \quad (37)$$

where $I(q)$ is now assumed to be in absolute units. Gerold (18) has shown that, for a binary alloy without size effects, in stable or metastable equilibrium, the invariant is related to the concentrations at the phase boundaries by

$$Q_o(\chi_I) = \frac{(\Delta f_B)^2}{V_A} (\chi_I - \chi_{I'}) (\chi_{II} - \chi_I), \quad (38)$$

where Δf_B is the difference between the scattering amplitudes of the solute B and solvent A, V_A is the atomic volume of solute A, χ_I is the atomic fraction of solute B in the alloy, and $\chi_{I'}$ and χ_{II} are the corresponding concentrations in the two stable or metastable phases. Lyon et al. (34) argued that the partial structure functions could be derived if additional measurements at a second edge were available. In a later work on these alloys, Lyon and Simon (35) concluded that in an Al-9 at.% Zn - 9 at.% Ag alloy, the ratio of Ag to Zn in the GP zones remained constant at about 1.10, but in an Al-14 at.% Zn - 4 at.% Ag alloy this ratio changed from 0.475 to 0.275 as the precipitates transformed from GP Zones to the stable ϵ' precipitate particles.

Building on the accumulated experience just noted, Simon and Lyon (42) and Lyon and Simon (36) reported the most comprehensive and successful partial structure function determination to date. Their anomalous small angle

scattering measurements were made near the K edges of Fe and Ni on a Cu-Ni-Fe alloy. They explored various approaches for extracting the partial structure functions. The method chosen was to obtain preliminary estimates of S_{ij} by direct inversion of a set of equations having the form of Eq. (36); these values were refined further by a gradient method. The method was shown to be reliable provided data in the vicinity of two absorption edges were used. Their partial structure factors for three annealing times at 500°C are shown in Fig. 8. The partial structure functions $S_{\text{Cu-Cu}}$, $S_{\text{Ni-Ni}}$ and $S_{\text{Fe-Fe}}$ were similar in shape, and their ratios did not vary with time; $S_{\text{Fe-Fe}}/S_{\text{Cu-Cu}} \cong 0.2 \pm 0.03$ and $S_{\text{Ni-Ni}}/S_{\text{Cu-Cu}} \cong 0.62 \pm 0.07$. Furthermore, they reached the important conclusion that phase separation at 500°C in the $\text{Cu}_{0.426}\text{Ni}_{0.422}\text{Fe}_{0.152}$ alloy cannot be modelled as a two-phase system. This has profound consequences in regards to our understanding of the process of phase separation. A satisfactory understanding of the exact nature of these precipitate particles may have to come from a higher resolution technique, such as field emission microscopy or perhaps from Monte Carlo modelling.

V. Discussion and Conclusions

Clearly, anomalous X-ray and resonance neutron scattering are capable of yielding valuable structural information, in addition to that obtainable from a conventional, off-resonance experiment. The methods, in essence, allow one to alter the scattering power of certain atoms in the scattering entity by use of appropriate wavelength radiation, in close proximity of an absorption edge. This is an inherent advantage relative to isotopic substitution alone since one is able to use the identical sample for all the necessary scattering experiments. The X-ray method has some advantage in that more absorption edges are readily accessible with available synchrotron sources. However,

there are a few isotopes that exhibit resonance in an energy range accessible with current pulsed neutron sources. Keeping in mind the complementary nature of X-ray and neutron scattering, this additional possibility should not be neglected, as will be discussed below.

As the works cited in section IV have repeatedly pointed out, anomalous small angle scattering experiments are demanding. Inasmuch as the signal available for interpretation is obtained from differences in scattering functions obtained with different wavelengths, counting statistics always become a limiting factor. Extreme precaution must be exercised to insure that systematic shifts in background levels are not introduced when the wavelength is changed; fluorescence must be corrected for; absorption is a major correction; and sample transmission should be measured for the same conditions of sample volume and wavelength used in the scattering experiment. Finally, reliable anomalous dispersion correction data (f' and f'') must be available, or determined as a part of the experiment.

Two major classes of experiments have been carried out to date using anomalous X-ray scattering methods; this work became feasible with the advent of synchrotron sources. These are macromolecules in solution and partial structure factors of metallic alloys. In both areas, research has progressed to the point that significant contributions have been made. Nonetheless, the era of anomalous small angle scattering is just commencing.

Resonance neutron scattering has been successfully applied for determining the crystal structure of insulin [Adams, et al.⁽¹⁾]. However, we are not aware of studies being reported for amorphous, metallurgical, or other macromolecular systems, certainly not in the small angle scattering regime. Possible reasons for the lack of such studies may be: (1). There are only a few isotopes which have resonance scattering properties in the thermal region

useful for small angle scattering, and they are not frequently found associated with the above mentioned classes of systems. (2). High flux, pulsed neutron sources with precisely tunable wavelengths over a wide range of energies have become available only recently. With the advent of such systems and time-of-flight analysis, one can optimize the resolution according to the system to be studied, and a number of unique experiments become possible. An obvious, partial list of systems for which resonance small angle scattering would appear to be applicable includes:

- (1) In biology, there are numerous proteins which function only when associated with certain metal species (e.g., calmodulin, phospholipase - A₂, hemoglobin, parvalbumin, metallothionin, etc.). It is possible to replace some or all of these metal species with resonance isotopes and then study their structures in terms of size, shape, and the distribution of the metal species.
- (2) In the field of solvent extraction of metals, a variety of extractants have been developed specifically to extract strategic materials, nuclear waste processing and recovery of certain radioactive nuclides.^(26,27) Depending on the conditions of extraction, a variety of complexes as well as larger aggregates are formed, and the aggregation properties of cobalt (II) - monoacidic extractant complexes were studied recently using conventional small angle neutron scattering techniques.⁽⁵¹⁾ Very little is known about the structures of aggregates or the distribution of atoms in these complexes.

- (3) In the fields of conventional metallurgy and polymers, microsegregation is known to influence dramatically the physical properties. If resonance labels can be introduced, the fine scale distribution can be characterized. Partial structure functions of phase separating systems can be used to obtain more reliable information about the bulk behavior.

Although no resonance small angle neutron scattering investigations have been reported to date, there is great potential for investigations of this type.

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Figure Captions

- Fig. 1. Wavelength dependence of (a) the real and (b) imaginary terms of the anomalous dispersion corrections for Fe near its K absorption edge. Numerical data taken from the calculation of Saravia and Caticha-Ellis⁽⁴⁰⁾ for f' and Cromer⁽¹⁰⁾ for f'' .
- Fig. 2. Measurements of (a) the real and (b) imaginary terms of the anomalous dispersion correction for Ni near its K absorption edge after Hoyt, de Fontaine, and Warburton.⁽²⁸⁾
- Fig. 3. Experimental values of (a) the real and (b) imaginary components of the anomalous dispersion correction for Cs near its L_3 edge after Templeton and Templeton.⁽⁴⁸⁾
- Fig. 4. Components of the coherent neutron scattering length:
(a) for ^{113}Cd calculated from the parameters from Brockhouse.⁽⁷⁾
(b) for ^{149}Sm calculated from the parameters from Marshak, Postma, Sailor, Shore, and Reynolds.⁽³⁷⁾
- Fig. 5. Guinier plot of the small angle scattering from rabbit parvalbumin (solid curve) compared with the curve calculated from the crystallographic coordinates of carp parvalbumin after Miake-Lye, Doniach and Hodgson.⁽³⁸⁾
- Fig. 6. Dependence of the apparent radius of gyration of ferritin on X-ray wavelength near the K absorption of Fe after Stuhmann.⁽⁴⁵⁾

Fig. 7. Direction of the tie lines in the Gibbs triangle for the Al-Zn-Ag system as determined by Lyon, Hoyt, Pro, Davis, Clark, de Fontaine, and Simon.⁽³⁴⁾

Fig. 8. Experimental partial structure functions for a Cu-Ni-Fe alloy after 3, 9, and 56 hours annealing at 500°C as reported by Lyon and Simon:⁽³⁶⁾ $S_{\text{Cu-Cu}}$ (open triangles), $S_{\text{Ni-Ni}}$ (open squares), $S_{\text{Fe-Fe}}$ (open circles) and $S_{\text{Ni-Fe}}$ (+).

















