

## On the Real Part of the Anomalous-Dispersion Term of Atomic Scattering Factors. II. Theoretical Part

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### Abstract

The real part of the anomalous-dispersion term is calculated by an approximate treatment which is equivalent to working from Pauli's equation. No use is made of the forward-scattering approximation. Although small  $\lambda$ -independent corrections are required, it turns out that the theory of Cromer & Liberman [*J. Chem. Phys.* (1970), **53**, 1891-1898] is essentially correct in accordance with the experiment of Saka & Kato [*Acta Cryst.* (1987), **A43**, 252-254]. The magnetic-scattering term [Jensen (1979). *Phys. Lett. A*, **74**, 41-44; (1980). *J. Phys. B*, **13**, 4337-4344] cannot be theoretically justified.

### 1. Introduction

In order to understand the experimental result of Saka & Kato (1987), the elastic-scattering amplitude is calculated with an approximation up to order  $(\hbar\omega/mc^2)^2$ , where  $mc^2$  is the rest energy of an electron and  $\hbar\omega$  is the energy of the incident photon. Since we are interested in diffraction experiments, forward scattering is not assumed. The theoretical scheme is close to that of Cromer & Liberman (1970) (hereafter CL) to ensure easy comparison. The principal result is that the magnetic-scattering term suggested by Jensen (1979, 1980) and Gerward, Thuesen, Jensen & Alstrup (1979) should not appear in accordance with the experimental result mentioned above.

In this paper, the notation  $f$  is used for the scattering amplitude, *i.e.* the scattering factor times the polarization factor. The same notation was used for the scattering factor in the previous paper, according to crystallographic tradition.

### 2. The relativistic formulation of the scattering amplitude

The elastic-scattering amplitude due to a single electron can be written in the form

$$f(\mathbf{s})/mc^2 = \sum_{n^+} \left( \frac{\langle a|X_1^*Q_2|n^+\rangle\langle n^+|Q_1X_1|a\rangle}{\varepsilon - \varepsilon_{n^+} + \hbar\omega + i\eta} \right.$$

$$\left. + \frac{\langle a|X_1Q_1|n^+\rangle\langle n^+|Q_2X_2^*|a\rangle}{\varepsilon - \varepsilon_{n^+} - \hbar\omega + i\eta} \right) + \sum_{n^-} \left( \frac{\langle a|X_2^*Q_2|n^-\rangle\langle n^-|Q_1X_1|a\rangle}{\varepsilon - \varepsilon_{n^-} + \hbar\omega} \right. \\ \left. + \frac{\langle a|X_1Q_1|n^-\rangle\langle n^-|Q_2X_2^*|a\rangle}{\varepsilon - \varepsilon_{n^-} - \hbar\omega + i\eta} \right) \quad (1)$$

where

$$\mathbf{s} = \mathbf{k}_1 - \mathbf{k}_2 \quad (2)$$

within the second-order perturbation approximation (Heitler, 1954). Here  $\mathbf{k}_1$  and  $\mathbf{k}_2$  are the wave vectors of the incident and scattered waves, respectively,  $|a\rangle$  indicates the state vector of an electron having relativistic energy  $\varepsilon$ ,  $n^+$  and  $n^-$  denote the intermediate state having positive and negative energy, respectively, and  $\eta$  is an infinitesimal constant due to the adiabatic approximation. The operators  $Q_i$  and  $X_i$  have the forms

$$Q_i = (\mathbf{e}_i \cdot \boldsymbol{\alpha}) \quad (3)$$

and

$$X_i = \exp(ik_i \cdot \mathbf{r}) \quad (4)$$

and  $\boldsymbol{\alpha}$  is the Dirac  $4 \times 4$  matrix which is related to the Pauli  $2 \times 2$  spin matrix  $\boldsymbol{\sigma}$  by

$$\boldsymbol{\alpha} = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & \mathbf{0} \end{pmatrix}. \quad (5)$$

The expression for  $f$  can be decomposed into three parts as

$$f = f_0 + (f^+ - f_0^+) + (f^- - f_0^-), \quad (6)$$

where the suffix 0 indicates the same expression as (1) except that the denominator is replaced by  $2mc^2$ , and the superscripts + and - indicate the terms  $\sum_{n^+}$  and  $\sum_{n^-}$ , respectively. Obviously,

$$f = f^+ + f^- \quad \text{and} \quad f_0 = f_0^+ + f_0^-.$$

It is easily shown that

$$f_0 = (\mathbf{e}_1 \cdot \mathbf{e}_2) \int \rho(\mathbf{z}) \exp(i\mathbf{s} \cdot \mathbf{r}) \, d\mathbf{r} \quad (7)$$

exactly and  $\rho(\boldsymbol{z})$  is the probability density of the electron in the state  $|a\rangle$ .

According to CL  $f^+$  is the leading term of the anomalous dispersion and the correction term has the form\*

$$\begin{aligned}\delta &= -f_0^+ + (f^- - f_0^-) \\ &= \frac{2}{3}E_{\text{tot}}/mc^2\end{aligned}\quad (8)$$

where  $E_{\text{tot}}$  means the total energy of an atom in the ground state. Jensen (1979), as briefly explained in the *Introduction* to paper I (Saka & Kato, 1987), criticized CL's result and showed that

$$f_0^+ = -\frac{2}{3}E_{\text{tot}}/mc^2 + \frac{1}{4}Z(\hbar\omega/mc^2)^2 \quad (9a)$$

$$f^- - f_0^- = E_{\text{tot}}/mc^2 - \frac{1}{4}Z(\hbar\omega/mc^2)^2. \quad (9b)$$

Obviously CL's correction is of order  $(v/c)^2$  and Jensen's (1979, 1980) additional term (magnetic scattering term) is of order  $(v_n/c)^4$ , where  $v$  and  $v_n$  are the velocities of electrons in the ground state and the intermediate state, respectively ( $mv_n^2 \approx \hbar\omega$ ). For this reason, if one needs Jensen's term, the whole calculation must be performed exactly up to order  $(v_n/c)^4$ . This is the main task in the following sections.

### 3. The higher-order calculation

The present approach is essentially equivalent to the Pauli approximation for (1) (Akhiezer & Beresteskii, 1965). The four components of a state vector are decomposed into two state vectors  $(\varphi, \chi)$ , each of which has two components. In the case of positive-energy states, they are related approximately as

$$\chi = (2mc)^{-1}(\boldsymbol{\sigma} \cdot \mathbf{p})\varphi \quad (10)$$

where  $\mathbf{p}$  is the momentum operator. The Hamiltonian operates on  $\varphi$  in the same manner as it does in Pauli's equation. If one neglects the spin-orbit coupling, it has the form

$$\mathbf{H} = [\mathbf{p}^2/(2m) + eV]\mathbf{1} \quad (11)$$

where  $eV$  means the potential energy and  $\mathbf{1}$  implies the  $2 \times 2$  diagonal identity matrix. For a negative-energy state,  $\chi$  and  $\varphi$  must be exchanged in (10) and the signs of  $\chi$  and  $eV$  must be reversed.

In addition, two assumptions have to be made for the ground state of the atom. First, the total sum of the spin along any specific direction is assumed to be zero. Next, the atom is assumed to be spherically symmetric. This implies that the total momentum of electrons in the atom is zero. Based on these assumptions the terms proportional to  $\boldsymbol{\sigma}$  and odd powers of  $\mathbf{p}$  will be dropped at a certain stage of calculation, although the formulation is referred to a single electron for convenience.

#### 3.1. The calculation of $f^- - f_0^-$

From (1) and the definition of the relevant term, one can obtain the expression

$$\begin{aligned}(f^- - f_0^-)/mc^2 &= \sum_n \langle a | X_2^* \mathbf{Q}_2 | n \rangle \langle n | \mathbf{Q}_1 X_1 | a \rangle \\ &\times \{ [2mc^2 + (E + E_n) + \hbar\omega]^{-1} - (2mc^2)^{-1} \} \\ &+ \sum_n \langle a | X_1 X_1 \mathbf{Q}_1 | n \rangle \langle n | \mathbf{Q}_2 X_2^* | a \rangle \\ &\times \{ [2mc^2 + (E + E_n) - \hbar\omega]^{-1} - (2mc^2)^{-1} \}\end{aligned}\quad (12)$$

where the superscript  $-$  is dropped in  $n^-$  for convenience, and  $\varepsilon$  and  $\varepsilon_n$  are replaced by  $E + mc^2$  and  $-(E_n + mc^2)$  respectively. Because  $mc^2 \gg (E + E_n) \pm \hbar\omega$ , the factor  $\{ \}$  can be approximated as

$$\begin{aligned}mc^2 \{ \} &= (-4mc^2)^{-1}(E + E_n \pm \hbar\omega) \\ &+ \frac{1}{2}(mc^2)^{-2}(E + E_n \pm \hbar\omega)^2 + \dots\end{aligned}\quad (13)$$

Incidentally, CL and Jensen took up only the first term.

First, let us calculate the summations

$$I_1 = \sum_n \langle a | X_2^* \mathbf{Q}_2 | n \rangle \langle n | \mathbf{Q}_1 X_1 | a \rangle (E + E_n + \hbar\omega) \quad (14a)$$

$$I_2 = \sum_n \langle a | X_1 X_1 \mathbf{Q}_1 | n \rangle \langle n | \mathbf{Q}_2 X_2^* | a \rangle (E + E_n - \hbar\omega). \quad (14b)$$

We shall omit the small terms proportional to  $|\varphi_n \chi_n|^2$  and assume that the  $\chi_n$  form a normalized complete set. If one recalls that  $E_n |\chi_n\rangle = \mathbf{H}_n |\chi_n\rangle$ , it follows that

$$I_1 = \langle \varphi_a | X_2^* (\mathbf{e}_2 \cdot \boldsymbol{\sigma}) (E + \mathbf{H}_n + \hbar\omega) (\mathbf{e}_1 \cdot \boldsymbol{\sigma}) X_1 | \varphi_a \rangle \quad (15a)$$

and the operator product can be reformed as

$$\begin{aligned}| \quad | &= X_2^* X_1 (\mathbf{e}_2 \cdot \boldsymbol{\sigma}) (\mathbf{e}_1 \cdot \boldsymbol{\sigma}) \\ &\times \{ \hbar\omega + (m)^{-1} [\mathbf{p}^2 + (\hbar \mathbf{k}_1 \cdot \mathbf{p}) + (\hbar \mathbf{k}_1)^2/2] \}.\end{aligned}\quad (15b)$$

In deriving this, the relations  $E|\varphi_a\rangle = \mathbf{H}|\varphi_a\rangle$ ,  $\mathbf{H} + \mathbf{H}_n = \mathbf{p}^2/m$  (for  $n = n^-$ ) and the commutative relation [(A2) of Appendix A] were employed. A similar expression is easily obtained for  $I_2$ .

The commutative and anticommutative relations (A4b, c) give the contributions of  $I_1$  and  $I_2$  to  $(f^- - f_0^-)$  in the form

$$\begin{aligned}\mathbf{I} &= (-4mc^2)^{-1}(I_1 + I_2) \\ &= \frac{1}{2}(\mathbf{e}_1 \cdot \mathbf{e}_2)(\hbar/mc)^2 \mathbf{g}(\mathbf{s}) \\ &\quad - \frac{1}{4}(\mathbf{e}_1 \cdot \mathbf{e}_2)(\hbar\omega/mc^2)^2 f_0(\mathbf{s})\end{aligned}\quad (16)$$

where

$$\mathbf{g}(\mathbf{s}) = \int \exp(i\mathbf{s} \cdot \mathbf{r}) \varphi_a^*(\mathbf{r}) \Delta \varphi_a(\mathbf{r}) \, d\mathbf{r}, \quad (17a)$$

$$f_0(\mathbf{s}) = \int \exp(i\mathbf{s} \cdot \mathbf{r}) \varphi_a^*(\mathbf{r}) \varphi_a(\mathbf{r}) \, d\mathbf{r}. \quad (17b)$$

In deriving (16), we have dropped a few terms proportional to  $\boldsymbol{\sigma}$  and  $\mathbf{p}$  for the reason mentioned above. In (17b),  $\varphi_a^* \varphi_a$  is not exactly the probability density  $\rho(\boldsymbol{z})$  used in (7). Since, however, the correction term

\* Equations (8), (9a) and (9b) refer to a single atom.  $Z$  is the number of electrons in the atom.

$\chi_a^* \chi_a$  is of order  $(v/c)^2$  and  $(\hbar\omega/mc^2)^2$  itself is of order  $(v_n/c)^4$ , it is safe to regard  $f_0$  as the scattering factor of an electron.

Next, we shall consider the higher-order terms,

$$\text{II}_1 = \sum_n \langle a | X_2^* Q_2 | n \rangle \langle n | Q_1 X_1 | a \rangle (E + E_n + \hbar\omega)^2, \quad (18a)$$

$$\text{II}_2 = \sum_n \langle a | X_1 Q_1 | n \rangle \langle n | Q_2 X_2^* | a \rangle (E + E_n - \hbar\omega)^2. \quad (18b)$$

In a similar manner to the case of (15a), for example,  $\text{II}_1$  has the form

$$\text{II}_1 = \langle \varphi_a | X_2^* (\mathbf{e}_2 \cdot \boldsymbol{\sigma}) (E + \mathbf{H}_n + \hbar\omega)^2 (\mathbf{e}_1 \cdot \boldsymbol{\sigma}) X_1 | \varphi_a \rangle. \quad (19)$$

In this case many terms appear, but after dropping the odd-power terms of  $\mathbf{p}$  and  $\boldsymbol{\sigma}$  and retaining the terms of order up to  $(v/c)^4$  and  $(v_n/c)^4$ , we have

$$\begin{aligned} \text{II} &= \frac{1}{8} (mc^2)^{-2} (\text{II}_1 + \text{II}_2) \\ &= \frac{1}{4} (\mathbf{e}_1 \cdot \mathbf{e}_2) (\hbar/mc)^4 G(\mathbf{s}) \\ &\quad + \frac{1}{4} (\mathbf{e}_1 \cdot \mathbf{e}_2) (\hbar\omega/mc^2)^2 f_0(\mathbf{s}) \end{aligned} \quad (20)$$

where

$$G(\mathbf{s}) = \int \exp(i\mathbf{s} \cdot \mathbf{r}) \varphi_a^*(z) \Delta^2 \varphi_a(z) d\mathbf{r}. \quad (21)$$

Finally, from (16) and (20) we obtain the result

$$f^- - f_0^- = (\mathbf{e}_1 \cdot \mathbf{e}_2) \left[ \frac{1}{2} (\hbar/mc)^2 g + \frac{1}{4} (\hbar/mc)^4 G \right]. \quad (22)$$

It is significant that the second terms in the expressions of I and II are exactly cancelled out.

### 3.2. The calculation of $f_0^+$

We start with the expression

$$\begin{aligned} f_0^+ &= \frac{1}{2} \left( \sum_n \langle a | X_2^* Q_2 | n \rangle \langle n | Q_1 X_1 | a \rangle \right. \\ &\quad \left. + \sum_n \langle a | X_1 Q_1 | n \rangle \langle n | Q_2 X_2^* | a \rangle \right). \end{aligned} \quad (23)$$

In this subsection and the next,  $n$  stands for  $n^+$ .

Let us consider the matrix element

$$\begin{aligned} M &= \langle n | QX | a \rangle \\ &= \langle \varphi_n | X(\mathbf{e} \cdot \boldsymbol{\sigma}) | \chi_a \rangle + \langle \chi_n | X(\mathbf{e} \cdot \boldsymbol{\sigma}) | \varphi_a \rangle. \end{aligned} \quad (24)$$

We shall omit the suffix for a while. By virtue of the relation (10) the smaller component  $\chi$  can be represented by the larger component  $\varphi$ . It follows then from the commutative relation (A1) and the properties (A4a, b) that

$$\begin{aligned} M &= (1/2mc) \langle \varphi_n | X(\mathbf{e} \cdot \boldsymbol{\sigma})(\mathbf{p} \cdot \boldsymbol{\sigma}) + (\mathbf{p} \cdot \boldsymbol{\sigma})(\mathbf{e} \cdot \boldsymbol{\sigma}) X | \varphi_a \rangle \\ &= (1/mc) \langle \varphi_n | \mathbf{A}X | \varphi_a \rangle \end{aligned} \quad (25a)$$

where

$$\mathbf{A} = (\mathbf{e} \cdot \mathbf{p}) - (i/2) \hbar (\boldsymbol{\sigma} \cdot [\mathbf{e} \times \mathbf{k}]). \quad (26)$$

It is easily seen that the conjugate matrix element has

the form

$$M^+ = \langle a | X^* Q | n \rangle = (1/mc) \langle \varphi_a | X^* \mathbf{A} | \varphi_n \rangle. \quad (25b)$$

If one includes the proper indices for  $M$ ,  $\mathbf{A}$ ,  $X$  etc. and assumes the completeness of  $\varphi_n$  one obtains\*

$$\begin{aligned} f_0^+ &= \frac{1}{2} (mc)^{-2} (\langle \varphi_a | X_2^* \mathbf{A}_2 \mathbf{A}_1 X_1 | \varphi_a \rangle \\ &\quad + \langle \varphi_a | X_1 \mathbf{A}_1 \mathbf{A}_2 X_2^* | \varphi_a \rangle). \end{aligned} \quad (27)$$

$\mathbf{A}_1$  and  $\mathbf{A}_2$  themselves are not commutable operators. Their order, however, can be exchanged under the average  $\langle \varphi_a | \quad | \varphi_a \rangle$  because the commutator results in only a term proportional to  $\boldsymbol{\sigma}$  [cf. equation (A4a)]. Thus in practice one can use the expression for the product

$$\mathbf{A}_2 \mathbf{A}_1 = \mathbf{A}_1 \mathbf{A}_2 = (\mathbf{e}_1 \cdot \mathbf{p})(\mathbf{e}_2 \cdot \mathbf{p}) + \frac{1}{4} (\hbar \mathbf{k})^2 (\mathbf{z}_1 \cdot \mathbf{z}_2) \quad (28)$$

where

$$\mathbf{z}_i = [\mathbf{e}_i \times \hat{\mathbf{k}}_i]. \quad (29)$$

It is worth noting that  $\mathbf{A}_i$  and  $X_i$  are commutable but  $\mathbf{A}_i$  and  $X_j$  are not [cf. equation (A3)]. Again, however, they are commutable under the average by dropping odd- $\mathbf{p}$  terms. From these relations, one obtains the expression

$$\begin{aligned} f_0^+ &= -\frac{1}{3} (\mathbf{e}_1 \cdot \mathbf{e}_2) (\hbar/mc)^2 g(\mathbf{s}) \\ &\quad + \frac{1}{4} (\mathbf{z}_1 \cdot \mathbf{z}_2) (\hbar\omega/mc^2)^2 f_0(\mathbf{s}). \end{aligned} \quad (30)$$

### 3.3. The calculation of $f^+$

Let us start with the expression

$$\begin{aligned} f^+ &= mc^2 \left[ \sum_n \langle a | X_2^* Q_2 | n \rangle \langle n | Q_1 X_1 | a \rangle \right. \\ &\quad \times (E - E_n + \hbar\omega + i\eta)^{-1} \\ &\quad + \sum_n \langle a | X_1 Q_1 | n \rangle \langle n | Q_2 X_2^* | a \rangle \\ &\quad \left. \times (E - E_n - \hbar\omega)^{-1} \right]. \end{aligned} \quad (31)$$

As in the case of  $f_0^+$ , with the use of the relation  $f(\mathbf{H}_n) | \varphi_n \rangle = f(E_n) | \varphi_n \rangle$ , it follows that

$$f^+ = J_1 + J_2 \quad (32a)$$

$$J_1 = (m)^{-1} \langle \varphi_a | X_2^* \mathbf{A}_2 \mathbf{B}^+ \mathbf{A}_1 X_1 | \varphi_a \rangle \quad (32b)$$

$$J_2 = (m)^{-1} \langle \varphi_a | X_1 \mathbf{A}_1 \mathbf{B}^- \mathbf{A}_2 X_2^* | \varphi_a \rangle \quad (32c)$$

where

$$\mathbf{B}^+ = (E - \mathbf{H}_n + \hbar\omega + i\eta)^{-1} \quad (33a)$$

$$\mathbf{B}^- = (E - \mathbf{H}_n - \hbar\omega)^{-1}. \quad (33b)$$

\* Note that the sign of the second term of (26) is negative in  $\mathbf{A}_1$  and positive in  $\mathbf{A}_2$ . In this manipulation,  $p_x^2 = p_y^2 = p_z^2 = \frac{1}{3} p^2$  has been used.

Inserting (26) into (32*b, c*) and dropping terms proportional to  $\sigma$ , one can see that each of  $J_1$  and  $J_2$  is decomposed into two components, *viz*

$$f^+ = J_1^p + J_2^p + J_1^m + J_2^m, \quad (34)$$

where

$$J_1^p = (m)^{-1} \langle \varphi_a | (\mathbf{e}_2 \cdot \mathbf{p}) X_2^* \mathbf{B}^+ X_1 (\mathbf{e}_1 \cdot \mathbf{p}) | \varphi_a \rangle \quad (35a)$$

$$J_2^p = (m)^{-1} \langle \varphi_a | (\mathbf{e}_1 \cdot \mathbf{p}) X_1 \mathbf{B}^- X_2^* (\mathbf{e}_2 \cdot \mathbf{p}) | \varphi_a \rangle \quad (35b)$$

$$J_1^m = \frac{1}{4} (\mathbf{z}_1 \cdot \mathbf{z}_2) (\hbar\omega)^2 (mc^2)^{-1} \langle \varphi_a | X_2^* \mathbf{B}^+ X_1 | \varphi_a \rangle \quad (35c)$$

$$J_2^m = \frac{1}{4} (\mathbf{z}_1 \cdot \mathbf{z}_2) (\hbar\omega)^2 (mc^2)^{-1} \langle \varphi_a | X_1 \mathbf{B}^- X_2^* | \varphi_a \rangle. \quad (35d)$$

The components with superscripts  $p$  and  $m$  are called the photoelectric- and magnetic-scattering terms, respectively.

First, we shall consider the magnetic-scattering terms (35*c, d*). In order to manipulate these some properties are needed of operators of the form  $X_i \mathbf{B}^\pm X_j$ , as outlined in Appendix B.

From (B4), then, one obtains

$$\begin{aligned} f_m^+ &= J_1^m + J_2^m \\ &= \frac{1}{4} (\mathbf{z}_1 \cdot \mathbf{z}_2) (\hbar\omega/mc^2)^2 f_0(\mathbf{s}) \end{aligned} \quad (36)$$

within the approximation of order  $(v_n/c)^4$ . This expression is identical to the second term of (30). Again, the magnetic-scattering term should not appear in the final expression of  $(f^+ - f_0^+)$ .

Next, we shall consider the photoelectric-scattering terms (35*a, b*). The treatment used for the magnetic scattering may not be applied because the commutative relation of  $\mathbf{B}$  and  $(\mathbf{e} \cdot \mathbf{p})$  results in a formidable expression. Moreover, in many problems, we are interested in the imaginary part of  $f^+$  as well. For these reasons, the standard approach is to use a dispersion relation of Kramers-Kronig type. For this purpose, it is convenient to return to an expression of a type similar to (31), *viz*

$$\begin{aligned} f_p^+ &= J_1^p + J_2^p \\ &= (1/m) \left[ \sum_n (X_2^* \mathbf{M}_2)_{an} (\mathbf{M}_1 X_1)_{na} \right. \\ &\quad \times (E - E_n + \hbar\omega + i\eta)^{-1} \\ &\quad \left. + \sum_n (X_1 \mathbf{M}_1)_{an} (\mathbf{M}_2 X_2^*)_{na} (E - E_n - \hbar\omega)^{-1} \right], \end{aligned} \quad (37)$$

where the operator  $\mathbf{M}_i$  is given by

$$\mathbf{M}_1 = (\mathbf{e}_1 \cdot \mathbf{p}), \quad \mathbf{M}_2 = (\mathbf{e}_2 \cdot \mathbf{p}). \quad (38)$$

Using the conventional relation in the limit  $(\eta \rightarrow 0)$ ,

$$\begin{aligned} (E - E_n + \hbar\omega + i\eta)^{-1} \\ = P(E - E_n + \hbar\omega)^{-1} - \pi i \delta(E - E_n + \hbar\omega), \end{aligned} \quad (39)$$

one can rewrite (37) in the form

$$\begin{aligned} f_p^+ &= (1/m) \left\{ P \sum_n \frac{E - E_n}{(E - E_n)^2 - (\hbar\omega)^2} \right. \\ &\quad \times [(X_2^* \mathbf{M}_2)_{an} (\mathbf{M}_1 X_1)_{na} + (X_1 \mathbf{M}_1)_{an} (\mathbf{M}_2 X_2^*)_{na}] \\ &\quad + P \sum_n \frac{\hbar\omega}{(E - E_n)^2 - (\hbar\omega)^2} \\ &\quad \times [(X_1 \mathbf{M}_1)_{an} (\mathbf{M}_2 X_2^*)_{na} - (X_2^* \mathbf{M}_2)_{an} (\mathbf{M}_1 X_1)_{na}] \\ &\quad \left. - (\pi/m) i \sum_n \delta(E - E_n + \hbar\omega) (X_2^* \mathbf{M}_2)_{an} (\mathbf{M}_1 X_1)_{na} \right\} \end{aligned} \quad (40a)$$

If one admits the reciprocity theorem on the scattering amplitude in every order of perturbation [*i.e.*  $f(\mathbf{k}_2, \mathbf{k}_1) = f(-\mathbf{k}_1, -\mathbf{k}_2)$ ],\* it follows that

$$(X_2^* \mathbf{M}_2)_{an} (\mathbf{M}_1 X_1)_{na} = (X_1 \mathbf{M}_1)_{an} (\mathbf{M}_2 X_2^*)_{na} \quad (41)$$

in the present case. Then (40) is simplified in the form

$$\begin{aligned} f_p^+ &= \frac{1}{m} \left[ P \sum_n \frac{2(E - E_n)}{(E - E_n)^2 - (\hbar\omega)^2} (X_2^* \mathbf{M}_2)_{an} (\mathbf{M}_1 X_1)_{na} \right. \\ &\quad \left. - \pi i \sum_n \delta(E - E_n + \hbar\omega) (X_2^* \mathbf{M}_2)_{an} (\mathbf{M}_1 X_1)_{na} \right]. \end{aligned} \quad (40b)$$

In general  $(X_2^* \mathbf{M}_2)_{an}$  and  $(\mathbf{M}_1 X_1)_{na}$  may not be real. If, however, the detailed balance theorem holds for the scattering amplitude [*i.e.*  $f(\mathbf{k}_2, \mathbf{k}_1) = f(\mathbf{k}_1, \mathbf{k}_2)$ ], which is true for atoms having inversion symmetry, one can assume that  $(X_2^* \mathbf{M}_2)_{an} (\mathbf{M}_1 X_1)_{na}$  is real. In this case, the mathematical structure of (40*b*) is identical to that in the case of forward scattering. Then, the Kramers-Kronig type of dispersion relation can be used although  $(X_2^* \mathbf{M}_2)_{an} (\mathbf{M}_1 X_1)_{na}$  cannot be identified straightforwardly as the cross section for photoelectric absorption. Since the details of manipulating (40*b*) to obtain the real and imaginary parts of  $f_p^+$  are described in the literature (*e.g.* Cromer & Liberman, 1970; Jensen, 1980) we shall not repeat them here.

Finally, we obtain the expression for the total scattering amplitude, (6), by putting together (22), (30), (34), (36) and (40*a*) or (40*b*). Then the anomalous-dispersion term is given by

$$\begin{aligned} f' + if'' &= \text{Re}(f_p^+) + i \text{Im}(f_p^+) + (\mathbf{e}_1 \cdot \mathbf{e}_2) \\ &\quad \times \left[ \frac{5}{6} (\hbar/mc)^2 g(\mathbf{s}) + \frac{1}{4} (\hbar/mc)^4 G(\mathbf{s}) \right], \end{aligned} \quad (42)$$

where  $\text{Re}$  and  $\text{Im}$  refer to real and imaginary parts, and  $g(\mathbf{s})$  and  $G(\mathbf{s})$  are defined by (17*a*) and (21) respectively.

\* Here, the polarization and spin notations are omitted for simplicity.

#### 4. Discussion and concluding remarks

Starting with the most general expression for the elastic-scattering amplitude based on the Dirac relativistic equation, we derived a concrete expression (42) for the anomalous dispersion. The approximation used is essentially equivalent to the Pauli approximation. Several correction terms must be amended to give the leading term  $f_p^+$  of (40a) or (40b), which is identical to the non-relativistic expression for anomalous dispersion due to photoelectric scattering. To be exact, however, the relativistic wave function has to be used to calculate the matrix element. This result is slightly different from the formulation given by Cromer & Liberman (1970), in which the leading term consists of  $f_p^+$  and  $f_m^+$ , one of the magnetic-scattering terms, in the present notation. However, they neglected the term  $f_m^+$  in the numerical calculation because the order of magnitude,  $(v_n/c)^4$ , is small.

In the present formulation, the correction terms were calculated approximately up to order  $(v/c)^4$  and  $(v_n/c)^4$ . This approach is free from the approximation of forward scattering or the so-called optical approximation [ $\exp(i\mathbf{k} \cdot \mathbf{r}) = 1$ ]. This is desirable because we are interested in the application to diffraction experiments of X-rays of ångström wavelengths.

As regards the correction terms, two points are worth mentioning. First of all, the magnetic-scattering term should not appear. In fact, it consists of four terms, two of which were calculated by Jensen (1979) in the case of forward scattering. They, however, are cancelled by the other two which are newly calculated in this paper. The cancellation is exact in any scattering direction and any direction of polarization. This result is in accordance with the recent experiment reported in Paper I (Saka & Kato, 1987) and with the old result (Takeda & Kato, 1978). Further evidence can be seen in the excellent agreement among the structure factors of Si reported independently by Saka & Kato (1986), Aldred & Hart (1973) and Teworte & Bonse (1984), after the observed values are corrected by CL values. The experiment of the first group was carried out with 0.4 Å X-rays whereas the latter two groups obtained the structure factors with Ag and Mo  $K\alpha_1$ .

The second point pertains to two  $\omega$ -independent terms, given by the square bracket in (42). The first term relates to  $\langle p^2 \rangle$  of an atom, which reduces to  $\frac{5}{3}E_{\text{tot}}/mc^2$  obtained by CL in the case of forward scattering. The second term relates to  $\langle p^4 \rangle$ , which would be very small. Theoretically, these terms have an  $s$  dependence. Another  $s$  dependence is also anticipated in the leading term,  $f_p^+$ . Any variation in these terms, however, is expected to be very small because the main contribution in any of them is due to  $K$  electrons which are spatially confined within  $\rho_0 = a_0/Z$  ( $a_0 =$  the Bohr radius). In the case of Si it

amounts to 0.038 Å. Moreover, one can obtain the explicit form of  $g(s)$  as

$$g(s) = g(0)[1 + 2(s\rho_0/2)^2]/[1 + (s\rho_0/2)^2]^2. \quad (43)$$

The deviation of  $g(s)/g(0)$  from 1 is less than 0.3% even for the 880 reflection of Si. Thus, one need not bother about the  $s$  dependence.

Incidentally, the experiment of Saka & Kato (1987) and similar types do not afford any critical information on the  $\omega$ -independent term for the very reason of the experimental principle. At present, it seems rather hard to obtain any experimental evidence on the  $s$  dependence of these correction terms so that one has to rely on the theoretical argument presented here.

In conclusion, theoretically the  $\omega$  dependence of the real part of the anomalous scattering comes out only through the photoelectric scattering term  $f_p^+$ . The additional correction must be  $\omega$  independent and practically  $s$  independent. Unless the absolute value is required with any higher precision, CL's values are most reliable and can be used for many purposes.

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#### APPENDIX A

##### Some commutative relations

$$(i) \quad [\mathbf{p}, X] = X(\hbar\mathbf{k}). \quad (A1)$$

$$(ii) \quad [\mathbf{p}^2, X] = X\{(\hbar\mathbf{k})^2 + 2(\mathbf{p} \cdot \hbar\mathbf{k})\}. \quad (A2)$$

$$(iii) \quad [\mathbf{A}_i, X_j] = 0 \text{ from } (\mathbf{e}_i \cdot \mathbf{k}_j) = 0. \quad (A3a)$$

$$(iv) \quad [\mathbf{A}_1, X_2^*] = -X_2^*(\mathbf{e}_1 \cdot \hbar\mathbf{k}_2). \quad (A3b)$$

$$(v) \quad [\mathbf{A}_2, X_1] = X_1(\mathbf{e}_2 \cdot \hbar\mathbf{k}_1), \quad (A3c)$$

where  $X_i$  and  $\mathbf{A}_i$  are defined in the text, equations (4) and (26).

$$(vi) \quad (\mathbf{a} \cdot \boldsymbol{\sigma})(\mathbf{b} \cdot \boldsymbol{\sigma}) = (\mathbf{a} \cdot \mathbf{b}) + i(\boldsymbol{\sigma} \cdot [\mathbf{a} \times \mathbf{b}]). \quad (A4a)$$

$$(vii) \quad (\mathbf{a} \cdot \boldsymbol{\sigma})(\mathbf{b} \cdot \boldsymbol{\sigma}) + (\mathbf{b} \cdot \boldsymbol{\sigma})(\mathbf{a} \cdot \boldsymbol{\sigma}) = 2(\mathbf{a} \cdot \mathbf{b}). \quad (A4b)$$

$$(viii) \quad (\mathbf{a} \cdot \boldsymbol{\sigma})(\mathbf{b} \cdot \boldsymbol{\sigma}) - (\mathbf{b} \cdot \boldsymbol{\sigma})(\mathbf{a} \cdot \boldsymbol{\sigma}) = 2i(\boldsymbol{\sigma} \cdot [\mathbf{a} \times \mathbf{b}]). \quad (A4c)$$

#### APPENDIX B

##### Approximate expressions involving $X_i B^\pm X_j$

By virtue of the relation (A2), one can easily see that

$$X_2^* B^+ X_1 = X_2^* X_1 [(E - H_n) + \hbar\omega - \Delta_1]^{-1}, \quad (B1a)$$

$$X_1 B^- X_2^* = X_1 X_2^* [(E - H_n) - \hbar\omega - \Delta_2]^{-1}, \quad (B1b)$$

where

$$\Delta_1 = (2m)^{-1}[2(\mathbf{p} \cdot \hbar\mathbf{k}_1) + (\hbar\mathbf{k})^2], \quad (B2a)$$

$$\Delta_2 = (2m)^{-1}[-2(\mathbf{p} \cdot \hbar\mathbf{k}_2) + (\hbar\mathbf{k})^2]. \quad (B2b)$$

The operators (B1) act directly on  $|\varphi_a\rangle$  so that  $E - H_n = H_a - H_n = 0$  in the case of  $n = n^+$ . Since

$(v/c) \ll 1$  and  $(v_n/c)^2 \ll 1$  can be assumed,  $\Delta_1/(\hbar\omega)$  and  $\Delta_2/(\hbar\omega)$  are much smaller than unity. With the use of the power series for the terms in square brackets in (B1), we have

$$X_2^* \mathbf{B}^+ X_1 = X_2^* X_1 (\hbar\omega)^{-1} [1 + (\Delta_1/\hbar\omega) + (\Delta_1/\hbar\omega)^2 + \dots], \quad (B3a)$$

$$X_1 \mathbf{B}^- X_2^* = X_1 X_2^* (\hbar\omega)^{-1} [-1 + (\Delta_2/\hbar\omega) - (\Delta_2/\hbar\omega)^2 + \dots]. \quad (B3b)$$

From these, it follows that

$$\langle \varphi_a | X_2^* \mathbf{B}^+ X_1 + X_1 \mathbf{B}^- X_2^* | \varphi_a \rangle = \langle \varphi_a | X_1 X_2^* | \varphi_a \rangle (mc^2)^{-1} [1 + (v/c)^2 + \dots], \quad (B4)$$

where odd terms of  $p$  are dropped.

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## Structure Factors and Debye Temperatures of Al–Li Solid-Solution Alloys

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### Abstract

By combining the accurate low-angle X-ray structure factors of Al–Li solid-solution alloys (containing 5.25 and 8.06 at.% Li) determined by the critical voltage technique in high-energy electron diffraction (HEED) with higher-angle values obtained by interpolation between best pure-element form factors, a complete set of accurate X-ray structure factors for these alloys has been produced. From the measured Debye–Waller factors for the alloys it was found to be difficult to determine a Debye temperature trend with composition for Al–Li solid-solution alloys because of the extent of the experimental errors, although the results suggest that the Debye temperatures of the alloys are higher than that of pure aluminium. This is obviously consistent with an increase in Young's modulus; *i.e.* the stiffness of the alloys appears to be greater than that of pure aluminium. This increase appears to arise predominantly from an increase in the force constant between nearest-neighbour (n.n.) lithium atoms in the alloy as compared with the value for pure lithium. This occurs because n.n. lithium atoms are closer together in Al–Li solid-solution alloys than they are

in pure lithium. Because the lithium atoms are closer together in the alloys, the electron charge density,  $\rho$ , associated with the valence electrons in the alloys is likely to be higher than if  $\rho$  is considered unchanged by alloying. This suggested increase in the charge density of the alloy valence electrons was confirmed, as the experimental 111 low-angle structure factors of the alloys were found to be significantly higher than the equivalent values obtained by interpolation between the best pure-element form factors. Such electronic changes are to be expected for Al–Li alloys as aluminium and lithium have a valency difference of two.

### 1. Introduction

When a crystal is set at a Bragg reflecting position in electron diffraction, the intensity of the diffracted beam is usually strong owing to the constructive interference of waves scattered in the diffracted-beam direction. However, for reflections higher than first order in a systematic row, at a particular electron accelerating voltage known as the critical voltage,  $V_c$ ,

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