

X-ray attenuation and anomalous scattering factors of medium-Z elements around their K edge

M. Kefi, J.-M. André, Y. Heno, G. Giorgi, and C. Bonnelle

Laboratoire de Chimie Physique, Université Pierre et Marie Curie, 11 rue Pierre et Marie Curie, F-75231 Paris CEDEX 05, France

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An analytic-calculation method enabling the evaluation of the real part of the anomalous scattering factor \bar{f}' from attenuation measurements in the x-ray range is presented. This method utilizes a power law to fit the variation of the experimentally observed mass attenuation coefficients as a function of the photon energy. It uses an analytic expression involving Gauss hypergeometric functions to calculate the dispersion term. A derivation of the relativistic correction to the dispersion term shows it to be smaller than the one used in the scattering-factor tabulation. The calculations using this method are tested for seven elements of medium Z : Pd, Ag, Cd, In, Sn, I and Xe, between 15 and 45 keV. Since they compare favorably with the *ab initio* calculation, the present approach can be considered as an advantageous alternative to the full calculation.

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I. INTRODUCTION

Accurate values of atomic scattering factors are important data for x-ray diffraction analysis and x-ray optical designs. Recent advances in theoretical techniques make it possible for photon scattering by bound electrons to be predicted, in principle, with a precision better than a few percent. Nevertheless, systematic disagreements remain between experimental scattering factors and theoretical predictions. Moreover, the more rigorous theoretical treatments are not sufficiently amenable to extensive systematic calculations because they necessitate the "exact" numerical resolution of complex quantum-electrodynamic programs. On the other hand, direct experimental measurements of the anomalous part of the scattering factor are difficult to perform; they use optical methods that are not operational beyond about 20 keV.

By using dispersion theory, the real part of the forward scattering factor for a photon of energy E_0 can be deduced from the dispersion integral over all frequencies of the attenuation cross section. The experimental evaluation of this integral requires knowledge of the attenuation spectrum for all frequencies. However, over the x-ray energy range, the scattering factor obtained by direct measurement is found to be in conflict with values derived from attenuation measurements via dispersion theory. Indeed, it is well known that the real part of the anomalous scattering factor is not properly described by dispersion theory but that relativistic correction terms to the dispersion relation must be included in the calculations.

The correction terms proposed by Cromer and Liberman (hereafter, CL) [1] and Jensen [2] are not in satisfactory agreement with recent optical measurements [3–5]. In the dipole approximation, CL propose for this correction term $-\frac{5}{3}E_{\text{tot}}/mc^2$, where E_{tot} is the total atomic binding energy and mc^2 is the electron rest energy. This CL value underestimates the real part of the anomalous scattering factor. However, this is the value used in the

most recent tabulations [6]. From an extension of the classical Thomas-Reiche-Kuhn sum rule to a Dirac electron, Levinger *et al.* [7] have proposed for the summed oscillator strength a correction term lower than that of CL. Systematic comparisons between theoretical values and accurate experimental data have suggested that the latter could be regarded as the most reliable term even for a many-electron system [8].

In this paper, we propose an analytical method to calculate the real part of the atomic anomalous scattering factor \bar{f}' from absorption data for any x-ray energy. For that purpose, we first consider in Sec. II the relation giving \bar{f}' as a function of the dispersion term and a relativistic corrective term for a single-electron atom. To compute the dispersion term in compact form, the absorption data must be under a functional form. Because no recent measurements of attenuation coefficients exist over the x-ray energy range [9–20], we have performed preliminary measurements for some medium- Z elements [21]. Later, these data were extended; they are presented in Sec. III for seven elements, Pd, Ag, Cd, In, Sn, I, and Xe, in the energy range between 15 and 45 keV, in terms of a power law E^{-n} , where n is a real number. In Sec. IV we describe the analytical method involving the Gauss hypergeometric functions proposed to compute the dispersion term with the help of this power law. Finally, by taking into account the correction term deduced in Sec. II, we determine in Sec. V the real part of the anomalous scattering factors for the seven elements. The precision is discussed as a function of uncertainties of experimental attenuation coefficients and of the extension of the integrated domain.

II. THEORETICAL BACKGROUND

In relativistic perturbation theory the scattering factor f for the forward electronic Rayleigh scattering by a single-electron atom is

$$f = mc^2 \left\langle i \left| \alpha \cdot \epsilon e^{ik \cdot r} \lim_{\gamma \rightarrow 0} \frac{\sum_n |n\rangle \langle n|}{\bar{E}_i - \bar{E}_n - \hbar\omega + i\gamma} \alpha \cdot \epsilon e^{-ik \cdot r} + \alpha \cdot \epsilon e^{-ik \cdot r} \lim_{\gamma \rightarrow 0} \frac{\sum_n |n\rangle \langle n|}{\bar{E}_i - \bar{E}_n + \hbar\omega + i\gamma} \alpha \cdot \epsilon e^{ik \cdot r} \right| i \right\rangle, \quad (1)$$

where $c\alpha$ is the Dirac velocity operator; ϵ , \mathbf{k} , and ω are, respectively, the polarization vector, the wave vector, and the angular frequency of the incident and scattered light. The ket $|i\rangle$ defines the state of the bound electron of energy $\bar{E}_i = mc^2 + E_i$ and

$$\sum_n |n\rangle \langle n| = \sum_{n^+} |n^+\rangle \langle n^+| + \sum_{n^-} |n^-\rangle \langle n^-|, \quad (2)$$

where $|n^+\rangle$ and $|n^-\rangle$ define intermediate electron states of positive and negative energy. The sums are taken over all positive and negative intermediate states except the positive energy states occupied by other atomic electrons. One has

$$\bar{E}_{n^+} = mc^2 + E_{n^+} \quad \text{and} \quad \bar{E}_{n^-} = -mc^2 - E_{n^-}. \quad (3)$$

We note

$$f = f^+ + f^-, \quad (4)$$

where f^+ and f^- are the terms with the sums on the positive and negative states, respectively.

In a nonrelativistic calculation including relativistic corrections to first order, the term f^+ is reduced to the usual nonrelativistic term

$$f^+ = f' - if'' \\ = \frac{1}{m} \left\langle i_{\text{NR}} \left| \epsilon \cdot \mathbf{p} e^{ik \cdot r} \frac{\sum_n |n_{\text{NR}}\rangle \langle n_{\text{NR}}|}{E_i - E_n - \hbar\omega} \epsilon \cdot \mathbf{p} e^{-ik \cdot r} + \epsilon \cdot \mathbf{p} e^{-ik \cdot r} \lim_{\gamma \rightarrow 0} \frac{\sum_n |n_{\text{NR}}\rangle \langle n_{\text{NR}}|}{E_i - E_n + \hbar\omega + i\gamma} \epsilon \cdot \mathbf{p} e^{ik \cdot r} \right| i_{\text{NR}} \right\rangle, \quad (5)$$

where the subscript NR refers to nonrelativistic states.

By taking into account the relation

$$\lim_{\gamma \rightarrow 0} \frac{1}{x + i\gamma} = P \frac{1}{x} - i\pi\delta(x), \quad (6)$$

where P denotes the Cauchy principal part and δ the delta function, the second term becomes

$$\frac{1}{m} \left\langle i_{\text{NR}} \left| \epsilon \cdot \mathbf{p} e^{ik \cdot r} P \frac{\sum_n |n_{\text{NR}}\rangle \langle n_{\text{NR}}|}{E_i - E_n + \hbar\omega} \epsilon \cdot \mathbf{p} e^{ik \cdot r} \right| i_{\text{NR}} \right\rangle - i \frac{\pi}{m} \left\langle i_{\text{NR}} \left| \epsilon \cdot \mathbf{p} e^{-ik \cdot r} \sum_n |n_{\text{NR}}\rangle \langle n_{\text{NR}}| \epsilon \cdot \mathbf{p} e^{ik \cdot r} \right| i_{\text{NR}} \right\rangle \delta(E_i - E_n + \hbar\omega). \quad (7)$$

By equalizing the real and imaginary parts, one obtains

$$(a) \quad f''(\omega) = \frac{\pi}{m} \sum_n |\langle n_{\text{NR}} | \epsilon \cdot \mathbf{p} e^{ik \cdot r} | i_{\text{NR}} \rangle|^2 \delta(E_n - E_i - \hbar\omega), \quad (8)$$

where f'' is the attenuation term; it is related to the attenuation cross section σ by the optical theorem

$$f''(\omega) = \frac{\omega}{4\pi c r_0} \sum_n \sigma_{i \rightarrow n}(\omega), \quad (9)$$

with r_0 the classical electron radius.

$$(b) \quad f'(\omega) = \frac{1}{m} \left\langle i_{\text{NR}} \left| \sum_n \epsilon \cdot \mathbf{p} e^{ik_n \cdot r} \frac{|n_{\text{NR}}\rangle \langle n_{\text{NR}}|}{E_i - E_n - \hbar\omega} \epsilon \cdot \mathbf{p} e^{-ik_n \cdot r} + \epsilon \cdot \mathbf{p} e^{-ik_n \cdot r} P \frac{|n_{\text{NR}}\rangle \langle n_{\text{NR}}|}{E_i - E_n + \hbar\omega} \epsilon \cdot \mathbf{p} e^{ik_n \cdot r} \right| i_{\text{NR}} \right\rangle, \quad (10a)$$

with

$$k_n = \frac{E_n - E_i}{hc} \quad \text{and} \quad \mathbf{k}_n = k_n \frac{\mathbf{k}}{k}. \quad (10b)$$

The dispersion term $[f'(\omega)]_{\text{disp}}$ is related to the imaginary part f'' of the scattering factor through the disper-

sion relation

$$[f'(\omega)]_{\text{disp}} = -\frac{2}{\pi} P \int_0^\infty \frac{\omega'}{\omega'^2 - \omega^2} f''(\omega') d\omega'. \quad (11)$$

In this relation, the integral is extended over the whole electromagnetic spectrum. It is easy to show that

$$f' = (f')_{\text{disp}} + \frac{1}{(mc)^2} \langle i_{\text{NR}} | (\boldsymbol{\epsilon} \cdot \mathbf{p})^2 | i_{\text{NR}} \rangle. \quad (12)$$

Then, f' differs from $(f')_{\text{disp}}$ by a correction term independent to the attenuation cross section, which is absent in the treatment by CL.

Finally, we obtain

$$f^+ = (f')_{\text{disp}} - if'' + \frac{1}{(mc)^2} \langle i_{\text{NR}} | (\boldsymbol{\epsilon} \cdot \mathbf{p})^2 | i_{\text{NR}} \rangle. \quad (13)$$

Next consider the term f^- . By assuming $\hbar\omega \ll 2mc^2$ and developing the operator relative to the states of negative energy up to second order, we get

$$\begin{aligned} \frac{1}{\bar{E}_i - \bar{E}_n - \pm \hbar\omega + i\gamma} &\approx \frac{1}{\bar{E}_i - \bar{E}_n - \pm \hbar\omega} \\ &= \frac{1}{2mc^2} - \frac{1}{(2mc^2)^2} (E_i + E_n - \pm \hbar\omega) \\ &\quad + \frac{1}{(2mc^2)^3} (E_i + E_n - \pm \hbar\omega)^2. \end{aligned} \quad (14)$$

The first term on the right-hand side corresponds to f_0^- ; the others correspond to $(f^- - f_0^-)_{\text{1st ord}}$, $(f^- - f_0^-)_{\text{2nd ord}}$, The term f_0^- (and also f_0^+) is obtained by replacing the matrix element denominators by $2mc^2$. Let us note that

$$f_0^+ + f_0^- = f_0, \quad (15)$$

where f_0 is the main part of the scattering factor which is equal here to 1 (or Z in the general case of an atom of atomic number Z).

We obtain

$$f_0^- = 1 - \frac{1}{(mc)^2} \langle i_{\text{NR}} | (\boldsymbol{\epsilon} \cdot \mathbf{p})^2 | i_{\text{NR}} \rangle - \frac{1}{4} \left[\frac{\hbar\omega}{mc^2} \right]^2, \quad (16a)$$

$$\begin{aligned} (f^- - f_0^-)_{\text{1st ord}} &= -\frac{1}{mc^2} \left\langle i_{\text{NR}} \left| \frac{p^2}{2m} \right| i_{\text{NR}} \right\rangle \\ &\quad - \frac{1}{4} \left[\frac{\hbar\omega}{mc^2} \right]^2, \end{aligned} \quad (16b)$$

$$(f^- - f_0^-)_{\text{2nd ord}} = \frac{1}{4} \left[\frac{\hbar\omega}{mc^2} \right]^2. \quad (16c)$$

Finally,

$$\begin{aligned} f^- &= 1 - \frac{1}{(mc)^2} \langle i_{\text{NR}} | (\boldsymbol{\epsilon} \cdot \mathbf{p})^2 | i_{\text{NR}} \rangle \\ &\quad - \frac{1}{mc^2} \left\langle i_{\text{NR}} \left| \frac{p^2}{2m} \right| i_{\text{NR}} \right\rangle - \frac{1}{4} \left[\frac{\hbar\omega}{mc^2} \right]^2. \end{aligned} \quad (17)$$

By introducing the total kinetic energy $\langle T \rangle$, which is related to the total energy of the atom by the virial theorem

$$\langle T \rangle = -\langle E \rangle, \quad (18)$$

we have

$$\left\langle i_{\text{NR}} \left| \frac{p^2}{2m} \right| i_{\text{NR}} \right\rangle = -\langle E \rangle, \quad (19)$$

$$\frac{1}{m} \langle i_{\text{NR}} | (\boldsymbol{\epsilon} \cdot \mathbf{p})^2 | i_{\text{NR}} \rangle = -\frac{2}{3} \langle E \rangle.$$

Then the scattering factor for a one-electron atom is

$$\begin{aligned} f &= f' - if'' + f^- \\ &= 1 + (f')_{\text{disp}} - if'' + \frac{1}{mc^2} \langle E \rangle - \frac{1}{4} \left[\frac{\hbar\omega}{mc^2} \right]^2. \end{aligned} \quad (20)$$

For a Z atom, the forward-scattering factor can be written

$$f \approx Z + (f')_{\text{disp}} + \frac{1}{mc^2} \langle E \rangle - if'' - \frac{1}{4} \left[\frac{\hbar\omega}{mc^2} \right]^2, \quad (21)$$

making the real part of the anomalous scattering factor equal to

$$\bar{f}' = (f')_{\text{disp}} + \frac{1}{mc^2} \langle E \rangle - \frac{1}{4} \left[\frac{\hbar\omega}{mc^2} \right]^2, \quad (22a)$$

with

$$\left[\frac{\hbar\omega}{mc^2} \right]^2 \ll 1. \quad (22b)$$

The correction to the dispersion term is lower than that proposed by CL. It agrees with the correction term proposed by Levinger *et al.*⁷ for the summed oscillator strength.

III. EXPERIMENTAL MEASUREMENTS

A. Apparatus

The experimental setup used in the present investigation is described in detail elsewhere [21]. It consists of 40-cm bent-crystal transmission spectrometer in the Cauchois geometry. The dispersive analyser is (100) mica for which the first order of Bragg reflection is predominant. The characteristics of the crystal, namely, dimensions and quality, determine the instrumental resolution at lower energies, up to about 20 keV. By assuming the crystal to be perfect, the width of the instrumental function is 10 eV at 20 keV.

The x-ray source is the bremsstrahlung emitted by a sealed x-ray tube with a tungsten anode, supplied by a highly stabilized generator; the voltage and the electron intensity have a stability better than 10^{-3} per 1% supply-voltage variation.

The detector is an ion-implanted passivated silicon crystal giving, at room temperature, an energy resolution $\Delta E = 2.6$ keV at 14.4 keV, i.e., sufficient to eliminate possible higher harmonics by means of an amplitude discriminator. This type of detector was preferred to a NaI(Tl) scintillator, in spite of its lower efficiency, because an anomalous response of the NaI crystal occurs in the vicinity of the iodine K threshold at 33.2 keV, that is, within the spectral range of interest. The linearity of the

detector response has been carefully checked; this characteristic is important in the vicinity of an absorption edge.

The spectrometer is computer controlled; repeated scans of each spectral region have been performed in various configurations: e.g., different positions of the sample and different thicknesses of absorber sheets.

B. Samples

The metallic elements are studied in solid state. The thicknesses of the absorbing screens vary from 30 to 46 μm ; the absolute values are known to a precision of about 1 μm , and the uniformity of the thickness is better than 1%. With these values for the thickness, the transmittance T , i.e., the ratio I/I_0 , where I and I_0 are, respectively, the intensities measured with and without a sample, ranges between 0.1 and 0.7 over the whole spectral range of interest.

Iodine is studied in aqueous solution of NaI (0.4 mol/l) prepared with doubly distilled water. The liquid is contained in a cell with plastic films which are highly transparent to x radiation. The effective thickness of the cell is 5 mm \pm 0.02 mm.

Xenon is studied in gas phase at room temperature; it is contained in a 112 mm \pm 0.02 mm long cell under a pressure of 190 Torr. The windows are beryllium foils. The samples are chemically pure and no correction has been applied to account for possible impurities.

C. Data acquisition

The spectra are recorded continuously between 15 and 45 keV in 50-eV steps. Above approximately 20 keV, the energy resolution is determined by the 30- μm aperture of the detector slit which is kept constant throughout the scan. This aperture gives an energy spread of 13 eV at 20 keV and 60 eV at 45 keV which is consistent with the value chosen for the step. Errors introduced by deviations from the mean thickness of the sample were reduced by measuring the transmitted intensity for several positions of the sample and by using different samples.

The acquisition is carried out in the following sequence: (i) background noise without radiation, (ii) transmission spectrum, (iii) incident radiation spectrum. The spectra are calibrated in wavelength from absorption edges of well-known wavelength. Wavelength is converted to energy by the relation

$$E(\text{keV}) \lambda(\text{\AA}) = 12.3981 \quad (23)$$

The energy precision depends on the spectral range and the absorption edge used for the calibration; it is 20 eV at the Ag K edge.

D. Results

The mass attenuation coefficient τ (expressed in cm^2/g) is given by the Beer-Lambert law

$$\tau = \frac{1}{\rho t} \ln \frac{1}{T} \quad (24)$$

where t is the mean thickness of the sample; ρ is the volumic mass under the conditions of measurement (it is

deduced from the data tabulated in the *Handbook of Physics and Chemistry* [22]); and $T = I/I_0$ is the transmittance, (I_0 is determined after subtraction of the background). At each energy, mean values of τ are obtained from a sequence of T values measured for a given sample. When more than one sample is used for a given element, an average $\langle \tau \rangle$ was calculated from the set of τ values.

The precision of the value of τ for a given energy depends on two types of errors: (i) the systematic errors due to the apparatus and to the method used and (ii) the errors due to uncertainties in the parameters of the relation (24). Systematic errors can arise from the presence of radiation that is scattered or re-emitted by the absorbant screen, or by any part of the apparatus, and reaches the detector. This effect decreases towards the lower energy, that is to say, with the increasing Bragg angle, because the scattered beam is clearly separated from the direct beam. Below 35 keV, we have assumed that an error of this type is not present when correct conditions of adjustment are respected. On the other hand, towards the higher energies, we have detected the presence of scattered and nondispersed radiation occurring at the detector. The presence of this radiation introduces a systematic error in the measurement of τ . In practice, we have limited the determination of the attenuation coefficient to the energies lower than a limit value that depends on the quality of optical adjustment. In all cases, the values measured beyond 41 keV have not been taken into account.

Accidental errors are due to the uncertainty on the thickness of the samples and the specific mass ρ which occurs in the calculation of τ from the relation (24). We have estimated the error on these two factors from a large number of measurements made with various samples, as mentioned above. A statistical analysis of the data gives the error to be $\pm 3\%$. The error on the transmittance T is negligible. The energy calibration of the spectrometer does not introduce noticeable error. In fact, one expects the precision to be better than for determinations performed at some discrete energies because the measurements are fairly continuous.

Then the precision on our values of τ is $\pm 3\%$. Figure 1 shows the experimental variation of τ versus the radiation energy for a 30- μm -thick In sample compared to the mass photoabsorption coefficient μ computed according to the variation law

$$\mu = KE^{-n} \quad (25)$$

where K and n are the parameters tabulated by Leroux and Think [23]. The rather good agreement between the two curves suggests that the total attenuation coefficient could practically follow a similar law in the spectral range of interest. Differences between the two curves may be due to scattering processes (Compton and Rayleigh) whose cross sections are not in the theory described by a power law. Figure 2 shows an estimation of the relative contribution of the scattering effects for two elements (Sn, I) among those being studied [24]. It appears that these effects remain small in the spectral range con-

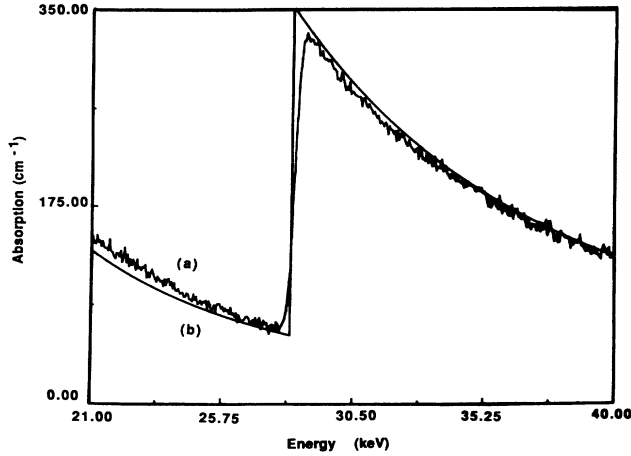


FIG. 1. Indium: (a) experimental mass attenuation coefficient and (b) mass photoabsorption coefficient computed from parameters tabulated in Ref. [23].

sidered, except just below the K edge where they amount to about 12% and they display a weak energy dependence, especially above the K edge. Thus, we have tentatively treated these scattering terms as if they could be included in the power law and set for the variation of the attenuation coefficient τ with E and λ ,

$$\ln[\tau(E)] = -n \ln(E) + C_E, \quad (26a)$$

$$\ln[\tau(\lambda)] = n \ln(\lambda) + C_\lambda. \quad (26b)$$

A logarithmic least-squares regression is used to determine the values of C_E (C_λ) and n on each branch of the curve, that is to say, on each side of the K threshold. The results are listed in Table I.

Our values of n are given with two decimal figures. It should be noted that many authors claim a much higher precision. In our opinion, there is some uncertainty on even the first decimal figure depending on the number of data used to perform the regression and on the extension of range. This is confirmed by the large dispersion of the published data which are generally obtained from measurements for only some discrete energies.

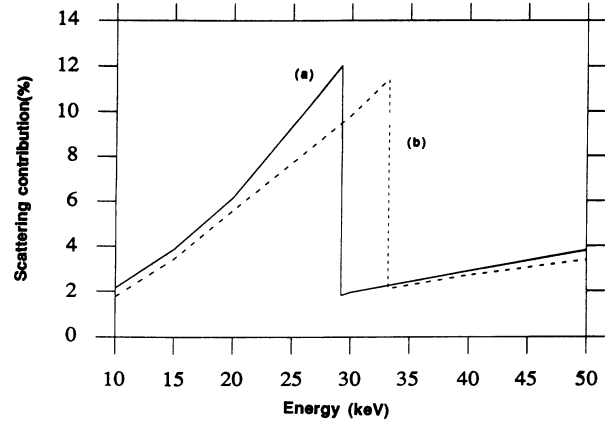


FIG. 2. Relative contribution of the scattering effects (Rayleigh and Compton) on the total attenuation cross section for Sn (a) and I (b), from Ref. [24].

IV. CALCULATION OF THE DISPERSION TERM

In terms of the mass attenuation coefficient τ at the photon energy E and by taking into account the relation (3), the imaginary part of the scattering factor is

$$f''(E) = \frac{A}{2hcr_0N} E \tau(E) \quad (27a)$$

$$= C_A E \tau(E), \quad (27b)$$

where A is the atomic mass and N is the Avogadro number.

Then the dispersion term is

$$[f''(E_0)]_{\text{disp}} = -C_A \frac{2}{\pi} \text{P} \int_0^\infty \frac{E^2 \tau(E)}{E^2 - E_0^2} dE. \quad (28)$$

The dispersion relation is strictly valid so long as the integration domain is rigorously the interval $[0, +\infty]$. In fact, the absolute values of the mass attenuation coefficient are not known with sufficient accuracy over the whole electromagnetic spectrum and the integral extension is truncated. The domain of integration must largely exceed the region of interest. We restrict the in-

TABLE I. Parameters (C_E, C_λ, n) of the power law fitting the measured attenuation coefficients for seven medium- Z elements.

Element	$E < E_K; \lambda > \lambda_K$			$E > E_K; \lambda < \lambda_K$		
	$10^3 C_E$	C_λ	n	$10^3 C_E$	C_λ	n
Pd	49.870	62.529	2.65	414.687	395.167	2.76
Ag	61.787	65.446	2.72	600.270	443.586	2.86
Cd	68.719	70.267	2.74	681.686	477.810	2.89
In	71.264	74.782	2.73	554.224	469.200	2.81
Sn	90.419	81.932	2.78	1102.644	593.340	2.99
I	77.344	94.327	2.67	750.427	586.129	2.84
Xe	85.151	97.514	2.69	1127.210	691.397	2.94

tegration domain to the x-ray region and compute the integral

$$J(E_0) = -C_A \frac{2}{\pi} \mathbf{P} \int_{E_\alpha}^{\infty} \frac{E^2 \tau(E)}{E^2 - E_0^2} dE, \quad (29)$$

$$J(E_0) = -\frac{2}{\pi} C_A \left[\sum_{q < K} \left[C_q \mathbf{P} \int_{E_q}^{\infty} \frac{E^{2-n_q}}{E^2 - E_0^2} dE - C_{q+1} \mathbf{P} \int_{E_{q+1}}^{\infty} \frac{E^{2-n_q}}{E^2 - E_0^2} dE \right] + C_K \mathbf{P} \int_{E_K}^{\infty} \frac{E^{2-n_K}}{E^2 - E_0^2} dE \right], \quad (30)$$

where q designates an occupied electronic inner shell other than K shell, and $q+1$ the occupied inner shell having an energy higher than q . E_q is the absorption-edge energy of the inner shell q and c_q, n_q are the parameters characteristic of the power law which describes the mass-attenuation-coefficient dependence versus the photon energy on the branch q . The calculation essentially reduces to the computation of the integral $\gamma(E_0, E_\alpha, n)$:

$$\gamma(E_0, E_\alpha, n) = \mathbf{P} \int_{E_\alpha}^{\infty} \frac{E^{2-n}}{E^2 - E_0^2} dE, \quad (31)$$

where n is a real number larger than unity. To do this, we can follow the method used by one of us in a previous paper [25]. It was shown that $\gamma(E_0, E_\alpha, n)$ can be expressed with the help of Gauss hypergeometric functions ${}_2F_1$:

$$\gamma(E_0, E_\alpha, n) = \left[-\frac{E_\alpha^{-2b}}{2b} \right] {}_2F_1(1, b; b+1; z^2) \quad (32a)$$

if one sets

$$b = \frac{n-1}{2}, \quad z = \frac{E_0}{E_\alpha}. \quad (32b)$$

The integral (31) is rapidly computed so long as the hypergeometric function is judiciously expanded:

(i) inside the unit disk $|z^2| < 1$, a simple series expansion is relevant:

$${}_2F_1(1, b; b+1; z^2) = b \sum_{p=0}^{\infty} \frac{z^{2p}}{(b+p)}. \quad (33)$$

(ii) Outside the unit disk $|z^2| > 1$, a change of variable $z \rightarrow z^{-1}$ together with an analytic continuation gives

$${}_2F_1(1, b; b+1; z^2) = bz^{-2} \sum_{p=0}^{\infty} \frac{z^{-2p}}{(1-b+p)} + \frac{\pi b}{\sin \pi b} (-z^2)^{-b}. \quad (34)$$

(iii) When $|z^2|$ becomes close to unity, the convergence of the series involved in (34) may be tedious; then it is convenient to perform an analytic continuation after the change of variable $z^2 \rightarrow 1-z^2$. After some algebra, it yields

where E_α denotes the low-energy integration threshold.

Using the experimental power laws which describe the energy dependence of the mass attenuation coefficient on each absorption branch, the preceding relation can be rewritten:

$$\begin{aligned} & {}_2F_1(1, b; b+1; z^2) \\ &= -b \ln(1-z^2) z^{-2b} \\ & - b(1-b) \sum_{p=0}^{\infty} \frac{b_p}{p!} (1-z^2)^p \\ & \quad \times \sum_{q=p}^{\infty} \frac{1}{(q+1)(q+b)}, \end{aligned} \quad (35)$$

where $b_p = \Gamma(b+p)/\Gamma(b)$ and Γ stands for the Γ function. From these relations, a computational algorithm can be built to obtain the dispersion term of the atomic scattering factors from the measurement attenuation coefficients.

V. DETERMINATION OF ANOMALOUS SCATTERING FACTOR FOR MEDIUM-Z ELEMENTS

From our experimental data and the computational procedure described above, we have calculated the real part of the anomalous scattering factor from relation (22a) for seven medium- Z elements in the energy range between 15 and 45 keV. Let us recall that $\langle E \rangle$ is the ground-state energy. Henke *et al.* [26] have given a convenient expression of E_{tot}/mc^2 as a function of the atomic number Z . Consequently, we express this term as follows:

$$\frac{E_{\text{tot}}}{mc^2} = -\frac{\langle E \rangle}{mc^2} \approx \frac{3}{5} 1.03 \times 10^{-4} Z^2 + \frac{3}{5} 2.19 \times 10^{-6} Z^3. \quad (36)$$

The integration domain for the computation of $J(E_0)$ is limited towards the lower energies by the M_V absorption edge and towards the higher energies by a criterion of convergence during the computational process of the series. The variation of the real part of the anomalous factor \bar{f}' is given for Pd, Ag, Cd, In, Sn, I, and Xe in Figs. 3(a)–3(g).

The precision on the anomalous factor depends on (i) the relative uncertainty of the attenuation coefficient and (ii) the extension of the integration domain. Figure 4(a) displays the precision on the anomalous factor due to a relative uncertainty of $\pm 5\%$ of the attenuation coefficient. The calculation is carried out for Ag. The first singularity at 25.5 keV coincides with the K edge, while the second one at 33.25 keV corresponds to a

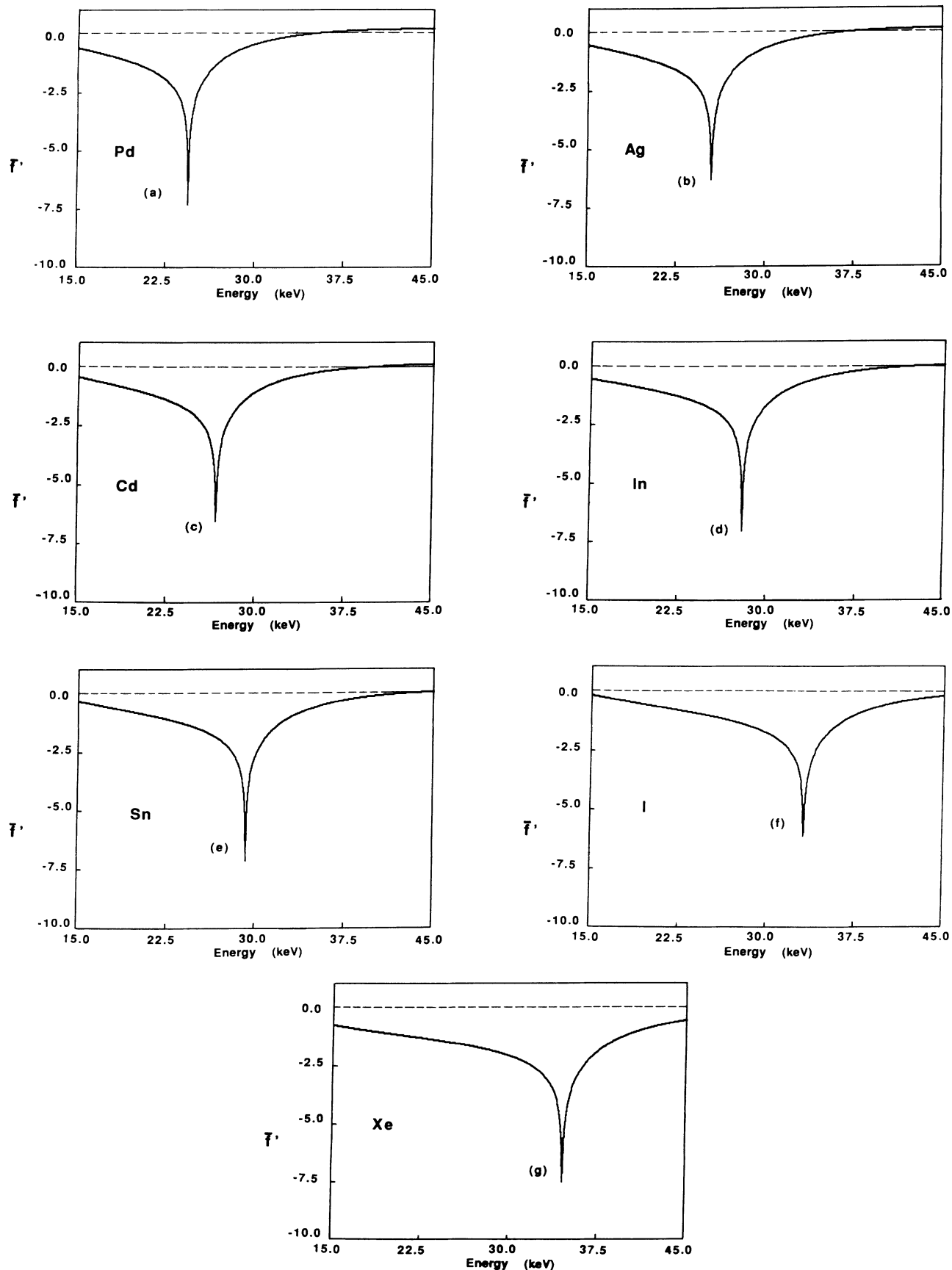


FIG. 3. Real part of the anomalous factor \bar{f}' : (a) Pd, (b) Ag, (c) Cd, (d) In, (e) Sn, (f) I, and (g) Xe.

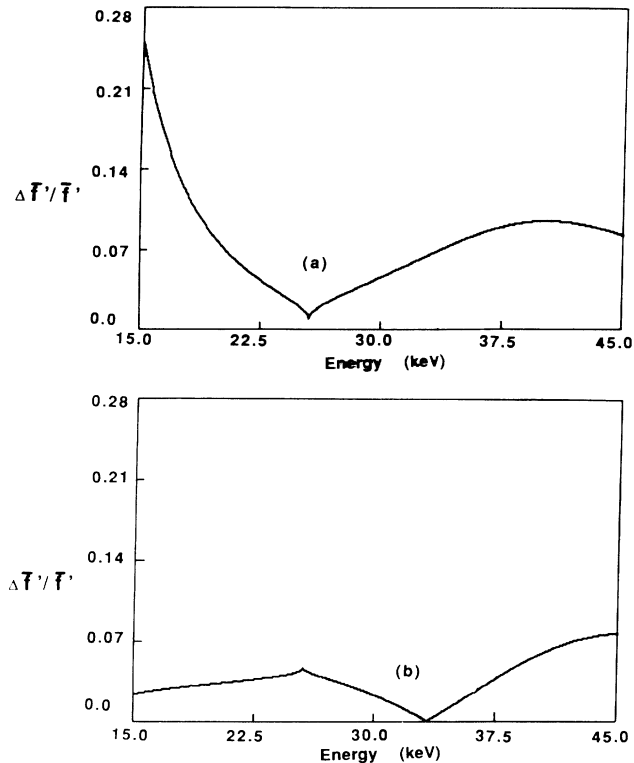


FIG. 4. Uncertainty on the anomalous factor of Ag due to: (a) uncertainty of τ and (b) extension of the integration domain.

change of sign in the quantity $f_{\tau \pm 5\%} - f_{\tau}$.

The choice of the integration domain may be more severe than the relative uncertainty of the attenuation coefficient. Figure 4(b) shows the relative error of the anomalous scattering factor computed for Ag resulting from an integration domain limited to the interval $[L_I - \infty]$ with respect to the integration domain extended to the M_V edge, that is, in the interval $[M_V - \infty]$.

Except for Sn and Xe above the K edge, the dispersion $(f')_{\text{disp}}$ in relation (1) is in close agreement with the real part of the anomalous term $(f^+)_{\text{CL}}$ computed from CL theory [1,6]. To make this assertion more quantitative, we report in Fig. 5, for Sn and I, the values of the real part of the anomalous factor tabulated by Sasaki from the CL theory [6] and using the corrective term

$$\Delta = -\frac{5}{3} \frac{E_{\text{tot}}}{mc^2} - \frac{1}{2} Z \left[\frac{E_0}{mc^2} \right]^2$$

and the data obtained from our computation method, to which we have added the same corrective term Δ for a direct comparison. Therefore, our semiempirical approach, which consists in fitting the total attenuation coefficient by a power law, is satisfactory. The discrepancy observed for Sn and Xe likely arises from a difference

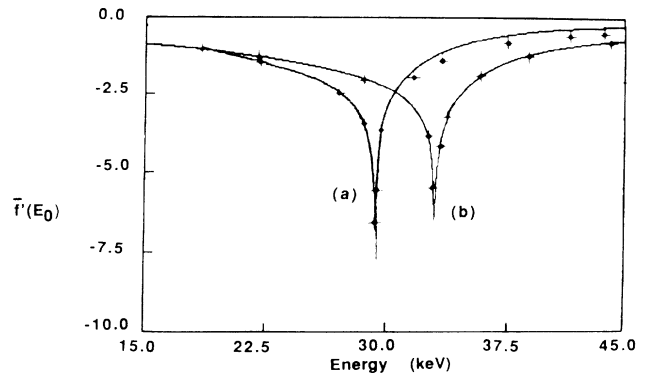


FIG. 5. Comparison between the dispersion term of the anomalous scattering factor obtained from our computation method (solid line) and the data (dots) tabulated by Sasaki [6] from the CL theory [1]. The data are for Sn (a) and I (b).

between our experimental measurements and the CL theoretical values; our computational method may not necessarily be incriminated. On the other hand, the real part of the anomalous term \bar{f}' is not directly comparable to the dispersion term $(f')_{\text{disp}}$ because of the presence of the corrective term. It follows that the ultimate accuracy in atomic factor calculated from attenuation coefficient values obtained either empirically or from *ab initio* calculations is closely dependent on this corrective term. The corrective term that we propose on a theoretical basis (see Sec. II) makes the values of the real part of the anomalous scattering factor in better agreement with the direct experimental (interferometric) determinations than the CL corrective term. This fact was previously discussed by Smith, especially for Si and Ca [8].

VI. CONCLUSION

It is known that a corrective term due to the relativistic and retardation effects must be added to the nonrelativistic real part $Z + (f')_{\text{disp}}$. On a theoretical basis, we propose for this term an expression different from that used in the recent tabulations of scattering factors: We find an agreement between this expression and the value expected from direct comparison between calculated and experimental values.

We have developed an analytical method to evaluate numerically the dispersion term from experimental attenuation coefficients. For this purpose the experimental absorption data are presented in a functional form. The variation of the attenuation coefficients as a function of the photon energy is fitted using a power law. This analytical treatment leads to values in agreement with those obtained by *ab initio* relativistic quantum calculations. This constitutes an interesting result because this method

can be implemented easily and does not require long computing time. Nevertheless, it must be emphasized that the precision of the proposed method depends both on the quality of the measurements and on the extension of the integration domain retained in the dispersion relation. By taking into account our proposed correction term and by using our simple computational method, it is possible to obtain rapidly and accurately the atomic scattering factors of a large number of elements in the x-

ray region; the method can be implemented as a routine in numerical codes for crystallography and optics.

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- [1] D. T. Cromer and P. Liberman, *J. Chem. Phys.* **53**, 1891 (1970).
- [2] M. S. Jensen, *Phys. Lett. A* **74**, 41 (1979).
- [3] A. Fontaine, W. K. Warburtar, and K. F. Ludwig, *Phys. Rev. B* **31**, 3599 (1985).
- [4] U. Bonse and M. Hart, *Appl. Phys. Lett.* **6**, 155 (1965).
- [5] C. Cusatis and M. Hart, *Proc. R. Soc. London, Ser. A* **354**, 29 (1970).
- [6] S. Sasaki, National Laboratory for High Energy Physics, Ibaraki-ken, 305, Japan, Report No. KEK 83-22 (unpublished).
- [7] J. S. Levinger, M. L. Rustgi, and K. Okamoto, *Phys. Rev.* **106**, 1191 (1957).
- [8] D. Y. Smith, *Phys. Lett. A* **123**, 200 (1987); *Phys. Rev. A* **35**, 3381 (1987).
- [9] L. H. Martin and K. C. Lag, *Proc. R. Soc. London, Ser. A* **137**, 199 (1932).
- [10] E. C. Stoner and L. H. Martin, *Proc. R. Soc. London* **1**, 107 (1925).
- [11] M. Cravy and J. H. Plassman, *Phys. Rev.* **153**, 307 (1967).
- [12] M. L. Wiedenbeck, *Phys. Rev.* **126**, 1009 (1962).
- [13] K. Gross Kurth, *Ann. Phys. (Leipzig)* **20**, 197 (1934).
- [14] Von Karl Shultz, *Ann. Phys. (Leipzig)* **27**, 1 (1930).
- [15] S. Laubert, *Ann. Phys. (Leipzig)* **40**, 553 (1938).
- [16] I. Muller, *Ann. Phys. (Leipzig)* **32**, 625 (1938); **35**, 524 (1939).
- [17] W. Wrede, *Ann. Phys. (Leipzig)* **36**, 681 (1939).
- [18] H. Hansen, *Ann. Phys. (Leipzig)* **35**, 524 (1939).
- [19] T. N. White, *Phys. Rev.* **46**, 865 (1934).
- [20] M. Kefi, J. M. André, and C. Bonnelle, *J. Phys. (Paris) Colloq.* **48**, C9-907 (1987).
- [21] J. M. André, M. Kefi, A. Avila, P. Couillaux, and C. Bonnelle, *Rev. Sci. Instrum.* **583**, 374 (1987).
- [22] *Handbook of Physics and Chemistry*, 55th ed., edited by Robert C. Weast (CRC, Cleveland, 1974).
- [23] J. Leroux and T. P. Think, *Revised Tables of X-Ray Absorption Coefficient* (Claisse Scientific Corporation, Québec, 1977).
- [24] J. H. Hubbell, *Photon Cross Sections, Attenuation Coefficients, and Energy Absorption Coefficients From 10 keV to 100 GeV*, Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 29 (U.S. GPO, Washington, D.C., 1969).
- [25] J. M. André, R. Barchewitz, A. Maquet, and R. Marmoret, *Phys. Rev.* **10**, 6576 (1984).
- [26] B. L. Henke, P. Lee, T. J. Tanaka, R. L. Shimabukwiv, and B. K. Fujikawa, *At. Data Nucl. Data Tables* **27**, 1 (1982).