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Sign reversal of the atomic scattering factor and grazing-incidence transmission at x-ray-absorption edges

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We investigate a conjecture that the atomic scattering factor may change sign as the result of strong dispersion near certain x-ray absorption edges. A corollary is that the refractive index of matter is greater than unity in such regions. We find probable examples at the $L_{\mathrm{II,III}}$ edges of aluminum and silicon. In these anomalous regions total external reflection at grazing incidence, which is characteristic of x rays, does not occur at any angle. Rather, there is unusually high transmission at grazing incidence for photon energies below the edge. This localized departure from total external reflection is a sensitive probe of optical properties and may possibly find application in thin-film notch filters for vuv or x-ray photons.

I. INTRODUCTION

The real part of the complex frequency-dependent refractive index $n(\omega)+ik(\omega)$ is normally less than unity for photon energies above the valence-electron plasma frequency ω_p (commonly 10–20 eV), i.e., for vacuum ultraviolet (VUV) and x-ray photons.[1] An important consequence of this is total external reflection [in the limit of $k(\omega)=0$] at an air or vacuum interface for all angles of incidence greater than the critical angle θ_c,

$$\sin\theta_c = n(\omega) , \tag{1}$$

where the angle of incidence θ is measured with respect to the normal to the surface. This characteristic of x rays was first discovered by Compton[2] in 1922 and is the basis for the reflective optical elements employed in x-ray telescopes[3] and synchrotron-light-source instrumentation.[4]

Speculations that $n(\omega)$ exceeds unity near some x-ray absorption edges have arisen from recent calculations by Henke *et al.*[5] of the complex atomic scattering factor which suggest that the real part of the scattering factor may become negative, contrary to conventional wisdom.[6] The connection of this sign change in the scattering factor to the index follows from the optical theorem,[7] which relates the atomic scattering factor[8] in the forward direction $f(\omega,0)=f_1(\omega,0)+if_2(\omega,0)$ to the complex dielectric function $\epsilon(\omega)$:

$$f(\omega,0)=(m\omega^2/4\pi Ne^2)[1-\epsilon^*(\omega)] . \tag{2}$$

In the x-ray range $n(\omega)\approx 1$ and $k(\omega)\ll 1$, so Eq. (2) may be expanded to yield the more familiar relations[9]

$$f_1(\omega,0)=(m\omega^2/2\pi Ne^2)[1-n(\omega)] , \tag{2a}$$

and

$$f_2(\omega,0)=(m\omega^2/2\pi Ne^2)k(\omega) . \tag{2b}$$

Here N is the atomic number density. Clearly, anomalous dispersion in $f_1(\omega,0)$ which is sufficient to drive the real part of the scattering factor negative would also yield values of the index $n(\omega)$ greater than unity.

It may be worth remarking that $f_1(\omega,0)$ must be negative over a substantial frequency range to satisfy the inertial sum rule.[10] Clearly, $f_1(\omega,0)$ is negative for $\omega<\omega_p$, where the refractive index is greater than unity. However, in principle, negative values can also occur in regions of strong anomalous dispersion at x-ray edges.

The resolution of the calculations of Henke *et al.*[5] is not sufficient to establish the details of the dispersion at the edges, but a sign change in $f_1(\omega,0)$ would have several intriguing consequences. For example, in such "anomalous" regions the intensity of forward x-ray scattering, which is proportional to $f_1(\omega,0)^2+f_2(\omega,0)^2$, would show extremely deep minima. This would make it possible to virtually extinguish the diffraction from selected atoms in a crystal-structure determination by appropriate selection of wavelengths. This tendency is already apparent in anomalous scattering near hard x-ray edges[1,11,12] where $f_1(\omega,0)$ becomes small, but remains positive.

The original speculation, which is explored here, is that the x-ray refractive index would be greater than unity over the small region near an x-ray edge at which the x-ray scattering factor has a negative real part. In such an "anomalous" range, total external reflection could not occur at any angle. Specifically, where $n(\omega)$ is nearly unity and $n(\omega)-1>0$, but $k(\omega)$ is small, there will be negligible reflection at all angles. On the other hand, in the "normal" regions which lie on either side of the "anomaly," the index remains less than unity and near total external reflection would occur at grazing incidence. Thus, an anomalous region would provide a wavelength window in a grazing-incidence mirror through which photons could pass into the material at all angles of incidence. Photons with energies above the edge would penetrate only a very short distance because of the high absorption coefficient, while those with energies below the edge should be transmitted through a relatively large thickness of material.

This effect should provide a sensitive probe of optical properties and it suggests the possibility of constructing a narrow-band notch filter. Such a transmission filter would be qualitatively similar to the transmission-mirror plus reflection-mirror filter studied by Bilderbach,[13] but would require only a single film and would not displace the photon beam significantly.

II. QUALITATIVE PHYSICAL PICTURE

Considerable insight may be gained from approximate classical considerations in which photon scattering from a system of bound electrons is divided into scattering from electrons with binding energies less than the incident photon energy and from those with binding energies greater than the photon energy. The former behave as though they were "free" and to a good approximation scatter according to the Thomson free-electron model.[1] The phase of the polarization attributable to these electrons lags the applied electric field by π at frequencies far above resonance, and they contribute to the dielectric function $\epsilon(\omega)$ according to[14]

$$\epsilon(\omega) \approx 1-(4\pi\mathcal{N}_{<}e^2/m)\omega^{-2} , \qquad (3)$$

where $\mathcal{N}_{<}$ is the integrated oscillator strength for all transitions below the energy $\hbar\omega$, provided ω is far from regions of significant absorption. In the classical limit $\mathcal{N}_{<}$ is just the number of electrons with binding energy below $\hbar\omega$.

The second group of electrons, those with binding energies significantly greater than the photon energy, behave as though they were "bound" electrons. They contribute an in-phase component to the polarization, but except in the region of anomalous dispersion near edges, this polarization is negligible relative to that of the "free" electrons.

This situation is illustrated for aluminum in Fig. 1 in which $n(\omega)-1$ derived[15,16] from experimental measurements by dispersion analysis is compared with the predictions of Eq. (3) using classical values of $\mathcal{N}_{<}$. In making this comparison the quantum-mechanical exchange of oscillator strength[17] between various core levels has been neglected. We have also used the fact that the complex dielectric function is nearly unity above ω_p so that for $\omega > \omega_p$ Eq. (3) yields

$$n(\omega)-1=\epsilon(\omega)^{1/2}-1 \approx -(2\pi\mathcal{N}_{<}e^2/m)\omega^{-2} . \qquad (4)$$

A similar comparison with classical values of $\mathcal{N}_{<}$ is made for the real part of the forward photon scattering factor $f_1(\omega,0)$ of aluminum in Fig. 2.

Despite the extreme degree of simplification inherent in Eq. 4, the approximation predicts the broad behavior of $n(\omega)$ above the valence-electron plasma frequency remarkably well ($\omega_p \approx 15$ eV in aluminum).

Exceptions to this simple picture occur at edges where the approximation fails badly, and below the plasma frequency where valence or conduction electrons give a strong, broad absorption. In these regions Rayleigh, i.e., resonant scattering,[1] must be taken into account. In particular, at x-ray edges the polarization involving energy levels responsible for the edge becomes very large and resonant effects dominate. At energies below an absorption edge, transitions to the states responsible for the edge are virtual and the polarization is in phase with the incident radiation, while well above the edge the transitions are real and the polarization is 180° out of phase with the incident field. Thus, the existence of a sign reversal in $f_1(\omega,0)$ below an absorption edge depends on whether or not the in-phase resonant polarization arising from near-edge transitions is sufficient to overcome the out-of-phase polarization from transitions at lower energies.

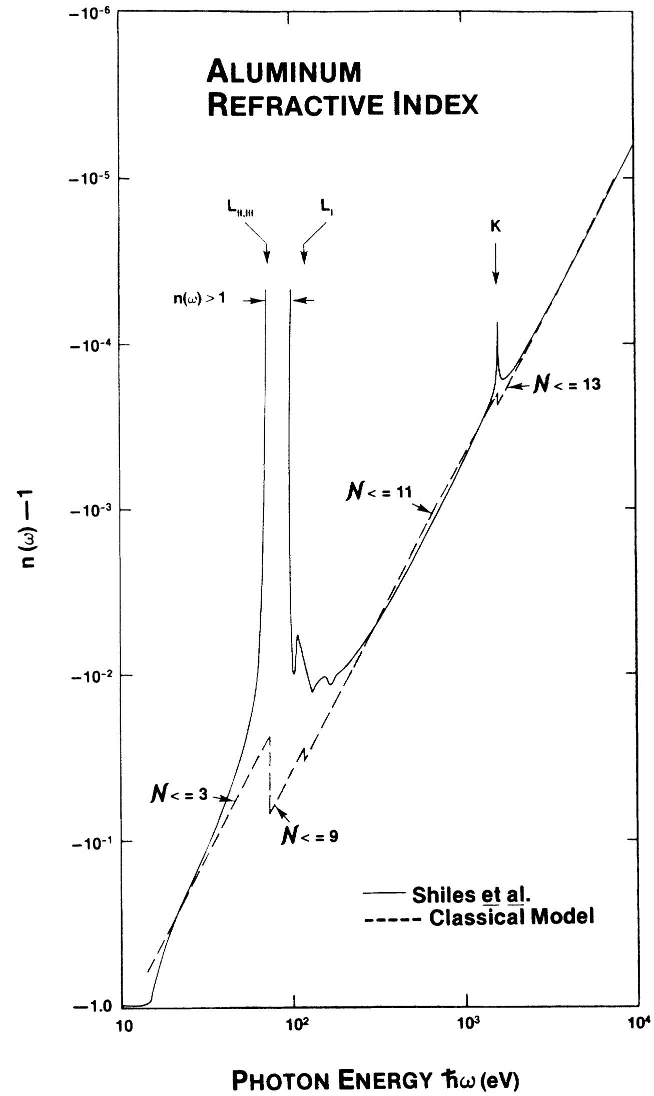

FIG. 1. The refractive index $n(\omega)$ for metallic aluminum plotted to emphasize the approximate power-law behavior of $n(\omega)-1$ between x-ray absorption edges, after Smith, Ref. 14. The dashed curve is based on a simple free-electron scattering model in which electrons with binding energies less than the photon energy scatter in the Thomson approximation, while those with greater binding energies make negligible contribution to the scattering.

III. CANDIDATE SYSTEMS

Conditions favorable for a sign change in the x-ray scattering factor include a strong absorption edge with a sharp onset to provide an in-phase "bound-electron" polarization comparable to the out-of-phase "free-electron" contribution. These conditions do not favor edges originating from levels with only a few electrons, especially *s*-like levels with but two electrons such as K, $L_{\rm I}$, $M_{\rm I}$, etc., edges. (A possible exception may be K edges in the second-period elements, which lack a well-developed L shell.) More likely candidates are $L_{\rm II,III}$,$M_{\rm IV,V}$, etc. edges which involve a large number of electrons.

Secondly, the edge in question must be sufficiently isolated that the high-energy absorption tails of transitions at lower energies are small at the edge. Otherwise, the jump ratio at the edge will not be large and the edge not sufficiently abrupt to give strong anomalous dispersion. Further, absorptions at lower energies must have sufficiently low total oscillator strength that their out-of-phase polarization does not overwhelm the in-phase component of the "bound-electron" transitions. These requirements do not favor the $3-d$ transition metals[18] in which a strong, broad M-shell absorption extends throughout much of the vuv. Together, these considerations suggest that the $L_{\rm II,III}$ edges of the third-period elements such as Al, Si, P, etc., are among the most favorable candidates for sign reversal of $f_1(\omega,0)$. Other possibilities include isolated $M_{\rm IV,V}$ edges in the fourth-period elements and K edges in the second period.

Unfortunately, there are few x-ray or vuv refractive index measurements with which to compare these speculations. Moreover, the estimated effect is beyond the accuracy of all but the most detailed direct theoretical calculations of $n(\omega)$. An alternative approach is dispersion theory which provides a means of analyzing experimental absorption data to obtain indirect "experimental" values of $n(\omega)$ and $f_1(\omega,0)$. Since absorption measurements at edges are notoriously difficult,[19] with uncertainties reaching factors of 2 or more, most dispersion analyses have avoided edge effects. Exceptions include recent dispersion studies of aluminum by Shiles *et al.*,[15,16] and of silicon by Shiles and Smith[20] and by Edwards.[21]

The dispersion theory results for the real part of the scattering factor $f_1(\omega,0)$ of aluminum[15,16] modified by the authors[22] to account for structure at the K edge, and the refractive index $n(\omega)$ of both aluminum[16] and silicon[20,21] are shown in Figs. 2–4. In these materials the index exceeds unity over a region some 30-eV wide about the $L_{\rm II,III}$ edge. Maximum values of $n(\omega)$ in this region are similar for both elements and range from 1.01_5 to 1.03_5 depending on the details of the analysis.

The real part of the scattering factor at these L edges is negative, with calculated extrema in the range of -4.4 to -5.5 in aluminum and from -4.2 to -9.8 in silicon (see Table I). These $f_1(\omega,0)$ values are particularly striking when compared to the Thomson (nonresonant) prediction of a scattering factor below the $L_{\rm II,III}$ equal to the number of electrons with binding energies less than the photon energy, i.e., the number of valence electrons—three

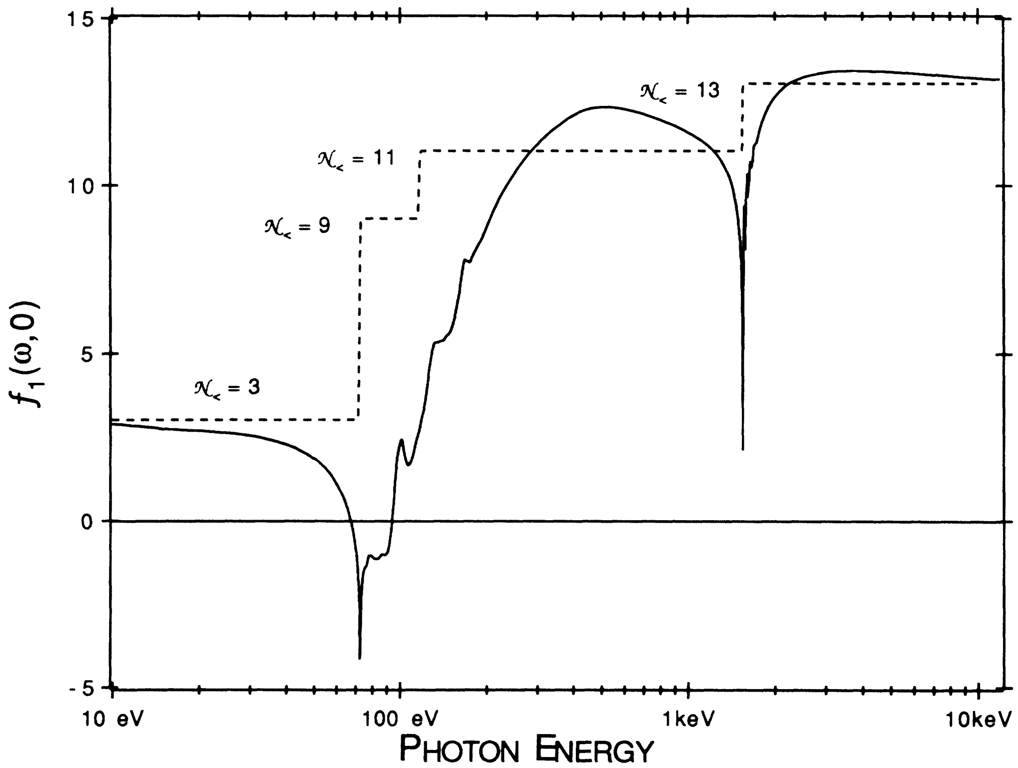

FIG. 2. The real part of the forward atomic scattering factor for aluminum as derived from the modified optical properties of Shiles *et al.*, Refs. 15, 16, and 22 (solid curve). The dashed curve indicates the result for the simple model in which only electrons with binding energies less than the photon energy scatter in the Thomson approximation.

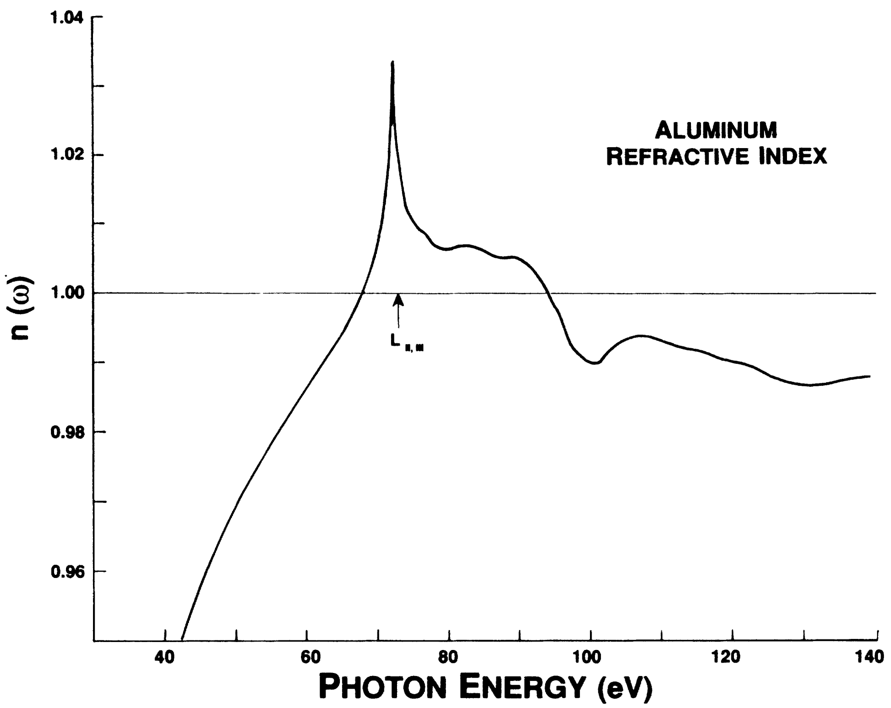

FIG. 3. The refractive index of metallic aluminum near the $L_{\mathrm{II,III}}$ edge after Shiles *et al.*, Ref. 15 and 16. The aluminum $L_{\mathrm{II,III}}$ edge lies at approximately 72.4 eV.

for aluminum and four for silicon.

We conclude that, at least in these elements, the in-phase resonant contribution to the polarization from the 2*p* electrons for photons with energies just below the $L_{\mathrm{II,III}}$ edge is roughly twice as strong as the out-of-phase contribution of the valence electrons. Thus, the sign of the scattering is reversed below the edge.

The strength of this sign reversal in aluminum and silicon suggests that a similar sign reversal should occur for other elements with a larger number of 3*p* electrons such as phosphorous, sulfur, etc. The first few elements in the fourth period are also possibilities. Potassium is a particularly interesting candidate because of the sharp absorption peak reported at the $L_{\mathrm{II,III}}$ edge.[23]

Our analysis of the absorption data gives no indication of a sign reversal at the *K* edge in either aluminum or silicon, in agreement with our qualitative discussion of *s* levels.

The calculated values for $n(\omega)$ and $f_1(\omega,0)$ at the minimum value of the scattering factor are summarized in Table I. To provide an estimate of the sensitivity of the dispersion results to small errors in the strength of

TABLE I. Extremal values of the refractive index $n(E_e)$ and the real part of the atomic scattering factor in the forward direction $f_1(E_e,0)$ for photons of energy E_e at the $L_{\mathrm{II,III}}$ and *K* edges of metallic aluminum.

		$L_{\mathrm{II,III}}$ Edge			*K* Edge	
	E_e (eV)	$n(E_e)$	$f_1(E_e,0)$	E_e (eV)	$n(E_e)$	$f_1(E_e,0)$
Aluminum						
with 14% reduction[a]	72.3	1.03_4	−4.4	1560	0.999 927	4.3 (1.9[b])
without reduction[c]	72.3	1.04_3	−5.5	1560	0.999 918	5.2
Silicon						
Shiles[d]	99.7	1.01_5	−4.2	1839	0.999 97	2.5
Edwards[e]	98.0	1.03_5	−9.8	1860[f]	0.999 93[f]	7[f]

[a] Reference 16.
[b] Reference 22.
[c] Reference 15.
[d] Reference 20.
[e] Reference 21.
[f] The mesh size of the published data is too great to locate this extremum accurately.

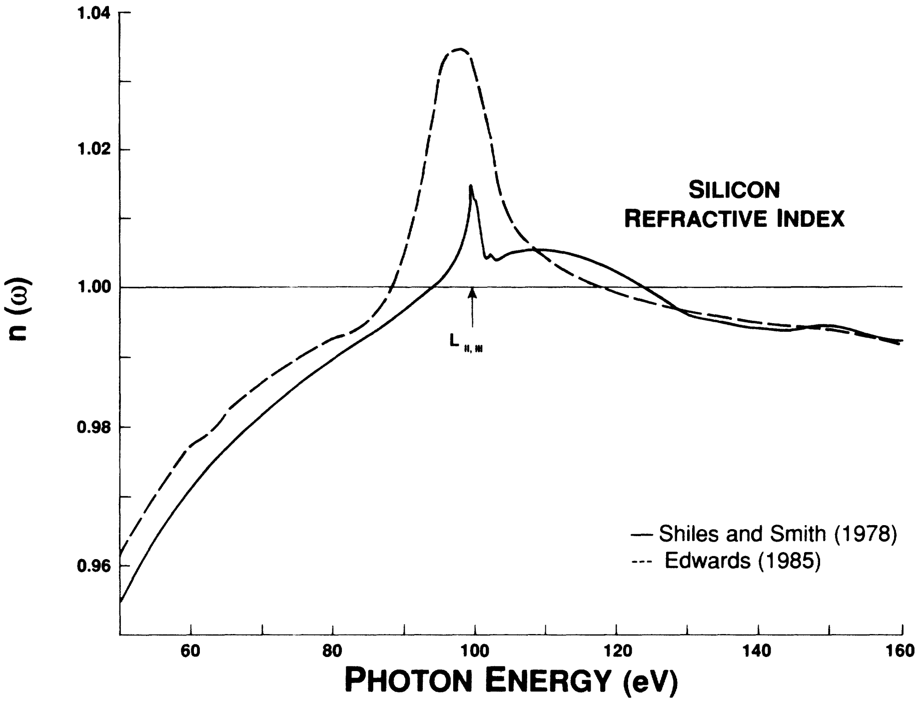

FIG. 4. The refractive index of crystalline silicon near the $L_{II,III}$ edge. The solid curve is taken from unpublished work of Shiles and Smith, Ref. 20. The broken curve follows the composite of Edwards, Ref. 21. The silicon $L_{II,III}$ edge lies at approximately 91.5 eV.

the $L_{II,III}$ absorption, two results are given: For aluminum they are taken from the published data of Shiles *et al.*,[15,16] which include a 14% reduction in the reported $L_{II,III}$ absorption (made to bring absorptions estimated from experimental measurements into conformity with the f-sum rule), and from the reported measurements without the 14% reduction. Similarly, for silicon the values are from the independent studies of Shiles and Smith[20] and of Edwards.[21] In all cases $f_1(\omega,0)$ is negative below the $L_{II,III}$ edge, and from this we conclude that the conjectured sign reversal in $f_1(\omega,0)$ is confirmed to well within the uncertainties of the absorption measurements.

IV. CONSEQUENCES

In terms of atomic scattering, the most striking feature of a minimum in $f_1(\omega,0)$ below an absorption edge is the deep minimum in the forward photon scattering amplitude, $f_1(\omega,0)^2+f_2(\omega,0)^2$. The effect is most evident below the edges where $f_2(\omega,0)$ is small and should be particularly pronounced where $f_1(\omega,0)$ has zeros. In condensed phases this minimum in atomic scattering appears as a sharp drop in reflectance and refraction at interfaces.

This is illustrated for the reflectance of a vacuum-aluminum interface near the $L_{II,III}$ edge for various grazing angles in Fig. 5. At both the $L_{II,III}$ and the K edges there are precipitous drops in reflectance. (The effect is not seen for the K edge in this figure since it is apparent at this edge only for angles of incidence of 89° or more.) In these regions of strong dispersion there is negligible reflection at all angles so that the relevant optical property is the transmission. This is given as a function of the angle of incidence for a 0.1-μm-thick aluminum film in Fig. 6.

At normal incidence such an aluminum film is partially transparent below both the L and K edges, but at grazing incidence—say for angles of incidence greater than 80°—it is a good reflector below 50 eV and from the

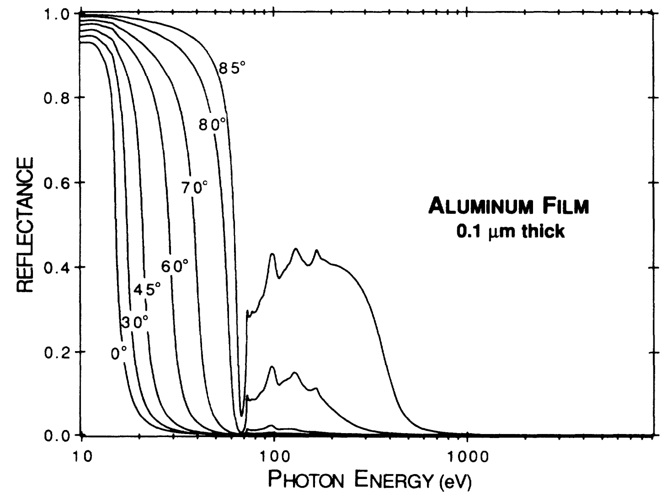

FIG. 5. The reflectance of an aluminum film 0.1-μm thick for s-polarized light at various angles of incidence as calculated from the optical constants of Shiles *et al.*, Ref. 15 and 16, but modified to include K-edge structure, Ref. 22.

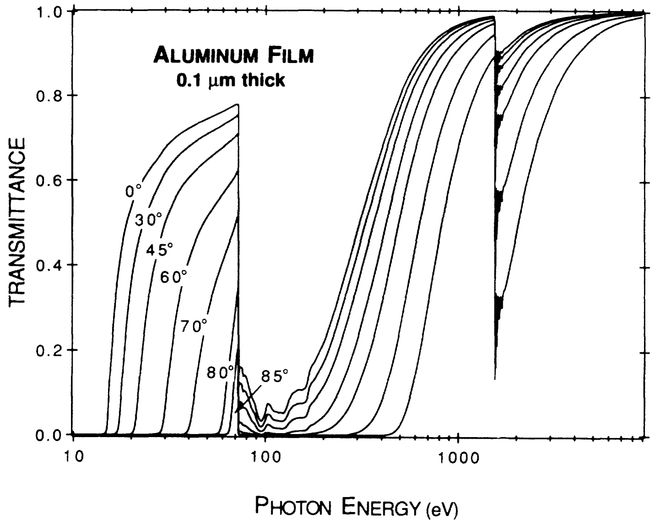

FIG. 6. The transmittance of a metallic aluminum film 0.1-μm thick for *s*-polarized light at various angles of incidence as calculated from the optical constants of Shiles *et al.*, Refs. 15 and 16, but modified to include *K*-edge structure, Ref. 22.

$L_{\mathrm{II,III}}$ edge to roughly 300 eV or beyond. However, for photon energies from approximately 60 eV to the $L_{\mathrm{II,III}}$ edge, there is a narrow window of particularly high transmission corresponding roughly to the region in which $n(\omega)\approx 1$ and $k(\omega)\ll 1$.

The reflectance and transmittance curves provide useful insights into the solution of Fresnel's equations for an absorbing thin film. This will be explored elsewhere. Here we stress that below the $L_{\mathrm{II,III}}$ edge there is not a sharp cutoff in transmission at photon energies for which the angle of incidence exceeds the critical angle θ_c. Rather, the curves are rounded with a small transmission extending toward lower energies as a result of the small absorptive component in the complex refractive index. However, extensions of the straight portion of the transmittance versus log energy curves in Fig. 6 (for a given value of θ) intercept the zero-transmittance axis at the energy for which the real part of the refractive index satisfies the critical angle condition (Eq. 1). In the absence of absorption there would have been an abrupt transition to total external reflection, and hence zero transmission, at this energy. Table II compares the intercept energy with the values of the index providing solutions of Eq. (1) for a given angle below the $L_{\mathrm{II,III}}$ edge. These results indicate that measurement of transmission as a function of angle can be used to infer the x-ray refractive index to a good approximations in "anomalous" regions of transparency where $n(\omega)>1$.

X-ray filters based on total external reflection have been proposed[13] and are especially attractive for use with high intensity sources, since they absorb little energy at unwanted wavelengths. However, total external reflection is achieved at typical x-ray edges only for small grazing angles necessitating long and narrow films in any practical device. On the other hand, total external reflection occurs at smaller angles of incidence for vuv and soft x-ray wavelengths. As demonstrated here for the aluminum and silicon $L_{\mathrm{II,III}}$ edges, there are regions of strong dispersion where the real part of the scattering factor varies rapidly with energy and actually changes sign. The result is a sharp transmission window bounded by regions of relatively high reflectance. Maximum transmissions of 40 to 50% are achievable suggesting that the effect could be exploited for notch transmission filters in the vuv and soft x-ray regions.

TABLE II. Correlation of the energy corresponding to a given critical angle θ_c with the energy at which the transmission extrapolates to zero in an aluminum film below the L edge. The former energy is the solution of $n(E)=\sin\theta_c$; in a nonabsorbing medium it is the upper limit of photon energies for total external reflection and, hence, zero transmission. The graphical determination of the energy intercept for zero transmission is good to approximately ±0.1 eV.

θ_c (degrees)	E for $n(E)=\sin\theta_c$ (eV)	Zero-transmission intercept (eV)
30	17.2	17.2
45	21.0	20.9
60	29.1	29.0
70	40.0	40.0
80	58.7	58.8
85	65.6	65.7

A tabulation of the calculated reflectance and transmittance of a 0.1-μm-thick aluminum film and the reflectance of an opaque aluminum surface for various angles of incidence has been deposited with the American Institute of Physics (AIP) Auxiliary Publication Service.[24]

Note added in proof. Eberhard Spiller has reported measurements of the refractive index of carbon in Co-C multilayers that show an index greater than unity over a 13-eV range near the *K* edge. The local maximum value reported is 1.0046 at 288 eV. This is in line with the conjecture in Sec. III of the present paper on possible sign reversals of the scattering factor at *K* edges of second-period elements. The amount by which the index exceeds unity at the carbon *K* edge is roughly one-seventh of that at the *L* edge of aluminum reported here. The relative sizes of these two effects is attributable in part to the larger number of electrons involved in the *L*-edge transitions. See E. Spiller, Brookhaven National Laboratory Report No. BNL 52176, 1988, p. 139.

ACKNOWLEDGMENTS

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[24] See AIP document no. PAPS PRBMDO-41-11 529-24 for 24 pages of calculated reflectance and transmittance as a function of angle for aluminum films. Order by PAPS number and journal reference from American Institute of Physics, Auxiliary Publication Services, 335 East 45th Street, New York, NY 10017. The prices are $1.50 for each microfiche (98 pages) or $5.00 for photocopies of up to 30 pages and $0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.