X-ray scattering factors of metallic aluminum calculated from a self-consistent x-ray attenuation data base

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The current best-fit tabulation of the optical absorption of aluminum is modified to include K-edge extended x-ray-absorption fine structure and other near-edge structures. The rationale used in choosing the most consistent K-edge data is discussed. Sum rules and comparisons with optical and electron-energy-loss experiments are used to check the consistency of the modifications to the absorption spectrum. The forward scattering factor is calculated from the modified spectrum and a significant difference in $f_1(\omega)$ is found between the original and the modified data sets near the K edge. This is largely due to resonant effects in the near-edge absorption structure of aluminum.

I. INTRODUCTION

Metallic aluminum has the distinction of being perhaps the most well studied of elements with regard to optical and electronic properties. Increasingly accurate composites of spectral data have been made over the years as more accurate measurements have become available.[1-5] In particular, previous work has resulted in a self-consistent absorption spectrum for aluminum from which the forward x-ray scattering factor may be calculated using dispersion analysis.[5,6] In this paper, we report values for the forward scattering factor over the vacuum ultraviolet (vuv) and x-ray range obtained by incorporating fine structure near the K edge of crystalline aluminum into the data base of Shiles et al.[5] Accurate knowledge of the dielectric-response function and scattering factors near absorption edges is of immediate interest for applications in x-ray and vuv optics. In addition, the methods developed are of intrinsic interest in that their application to a simple metal such as aluminum points the way toward better determination of the optical properties of more complex metals.

II. PROCEDURE

Neglecting spin-flip processes, the Kramers-Kronig relation[7] connecting the real and imaginary parts of the forward-scattering factor $\hat{f}(\omega) = f_1(\omega) + if_2(\omega)$ can be written as

$$f_1(\omega) = -\frac{2}{\pi}\omega^2 P \int_0^\infty \frac{f_2(\omega')}{\omega'(\omega'^2 - \omega^2)} d\omega . \tag{1}$$

Using the optical theorem[8] to express f_2 in terms of the linear mass absorption coefficient μ allows one to rewrite Eq. (1) as[9,10]

$$f_1(\omega) = -\frac{2}{\pi}\left[\frac{mpc}{4\pi Ne^2}\right]\omega^2 P \int_0^\infty \frac{\mu(\omega')}{(\omega')^2 - \omega^2} d\omega , \tag{2}$$

where N is the number density of atoms in the material, ρ is the mass density, and e and m are the electronic charge and mass, respectively.

Equations (1) and (2) are derived from the so-called optical form of the Kramers-Kronig relation for n and k.[11,12] The low-energy limit of Eq. (2) is constrained such that $f_1(0) = 0$. While this dispersion relation is perfectly correct, in practice it can be misleading in the calculation of dispersion in the x-ray region, since all errors in the absorption oscillator strength between $\omega = 0$ and the energy of interest combine to give the major portion of the error in the calculated forward-scattering factor.[11] For this reason, it is common in high-energy physics and in x-ray scattering theory to use a subtracted form of the dispersion relation that is pinned at $f_1(\infty)$.[11] This eliminates cumulative error from low-energy regions at the price of a good knowledge of the high-energy limit of f_1. For aluminum the classical value of this limit,

$$\lim_{\omega \to \infty} f_1(\omega) = Z , \tag{3}$$

where Z is the atomic number, is sufficient for our purposes. In more precise studies,[13,14] relativistic and multipole corrections to the Thomson scattering cross section must be included, in which case

$$\lim_{\omega \to \infty} f_1(\omega) = Z + \Delta , \tag{4}$$

where to lowest order

$$\Delta \approx \frac{E_{tot}}{mc^2} . \tag{5}$$

Here E_{tot} is the total atomic ground-state binding energy (a negative quantity). For aluminum the value of Δ is -0.013 yielding a value of 12.987 for $f_1(\infty)$.

The previous studies of Shiles et al.[5] provide an absorption data base for metallic aluminum that is free enough from uncertainties in the oscillator strengths that both the optical and the x-ray form give essentially the same result for the forward-scattering factor. As has been discussed elsewhere,[11,12,15] the fact that the two forms of the dispersion relation agree is equivalent to saying that the Thomas-Reiche-Kuhn f sum rule is satisfied by the absorption spectrum. In the present study the use of the subtracted dispersion relation was not necessary

since the absorption data obeyed the f sum rule to within experimental error.

III. MODIFICATIONS
TO THE K-EDGE SPECTRUM

In the work of Shiles and co-workers[5,16] no attempt was made to include extended x-ray absorption fine structure (EXAFS) and other near-edge effects at the K edge of aluminum. There were several reasons for this, not the least of which was that, at the time, detailed K-edge measurements were lacking. In the present study, we have compared a number of EXAFS and other near-edge structure measurements and then fit them into the frame provided by Shiles and co-workers.[5,16]

Shiles's spectrum is internally consistent, correctly satisfies the f sum rule, and the resulting dispersion analysis gives values for the optical constants that generally agree well with experiment. These data are also in agreement with the cross sections reported in previous compilations.[17,18] In short, the shape of the K-edge absorption that we use as a starting point lacks fine structure but is otherwise correct on a gross scale, and modifications to the edge must continue to satisfy sumrule tests and not conflict with data in other spectral regions. These constraints can serve as a powerful guide in deciding which measurements of the K-edge structure to include.

All of the high-resolution K-edge measurements of sufficient accuracy and range for our purposes were made using either synchrotron radiation[19−21] or radiation from a laser-produced plasma.[22−26] There are also data from electron-energy-loss measurements,[27] although the energy resolution is not equal to that of the best measurements using synchrotron or plasma sources.

The transmission near the K edge is usually reported as relative, not absolute values, so that the near-edge absorption data generally had to be scaled to splice it into the absorption data base. Of the absolute measurements, only a few[19,20,22] yield consistent absorption spectra when combined with the comprehensive data base. Our procedure for matching data sets was to scale the relative measurements to fit the absolute values for the continuum absorption 200–300 eV above the edge as derived from conventional measurements. Unfortunately, many EXAFS and near-edge measurements do not extend to high enough energies to make this possible.

The laser-produced plasma results for aluminum[22−26] appear to have unique problems, in addition to difficulties, such as scaling, that they share with synchrotron measurements. In particular, Eason et al.[24] have pointed out that there are discrepancies in the energy calibration and scaling between laser-plasma-derived data sets of different researchers.[22−26] This difficulty can be resolved by identifying known structures in the near-edge spectrum in order to select an EXAFS spectrum with a reasonably correct energy scale.

Since the initial state for K-edge transitions is s like, the major features of the absorption spectra from a few eV to at least 30 eV above the K edge follow the p density of states above the Fermi level in a one-electron picture. From augmented plane wave (APW) calculations of the
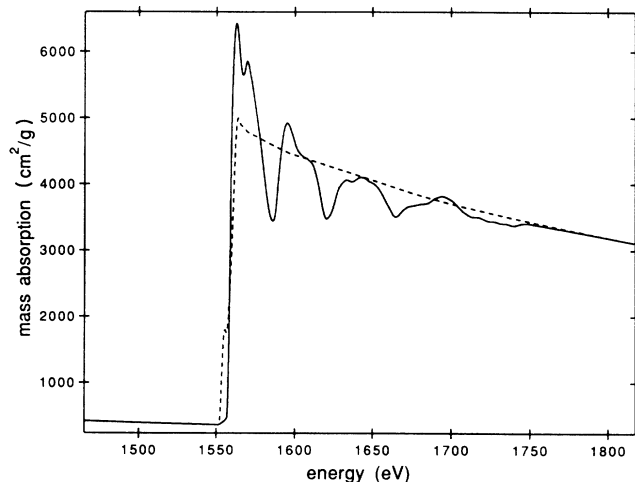

FIG. 1. Mass absorption coefficient as a function of energy at the K edge of metallic aluminum. The solid curve represents the present work and the dashed curve is from Shiles et al. (Refs. 5 and 6).

K-edge spectra[28,29] one expects to find an appreciable dip in the absorption approximately 28 eV above the K edge. This has been observed in near-edge spectra of aluminum measured with both synchrotron radiation[19] and standard tube sources,[30,31] as well as in electron-energy-loss spectra.[27] We used the position of this easily observed and well-defined minimum in the absorptance to discriminate between the various data sets.

The room-temperature synchrotron-radiation measurements made by Kiyono et al.[19] were judged to best fulfill the above criteria and were chosen to complete the K-edge absorption spectrum. These experiments agree well with the near-edge structure measurements, the position and magnitude of the EXAFS peaks, and showed a continuum absorption 200–300 eV above the K edge that is consistent with tube-source measurements[31] and theory.[32] The resulting modified K-edge spectrum is shown along with the spectrum from Shiles et al. in Fig. 1.

IV. OTHER MODIFICATIONS

In the process of calculating f_1 from the absorption spectra we noticed that additional changes to the absorption spectrum derived from Shiles et al. were necessary in spectral regions other than near the K edge. The data of Shiles et al.[5] contain small discontinuities in slope of $\mu(\omega)$ below the L edge and between the K and L edges. These produce anomalous "wiggles" in the calculated $f_1(\omega)$. However, examination of the original sources used by Shiles et al. suggests this arose primarily from round-off error in tabulation of the spectra. Moreover, one does not expect structure in the photoelectric cross section except near edges. Hence, we smoothed the Shiles data from 300 to 1500 eV by fitting their curve of $\mu(\omega)$ to the polynomial

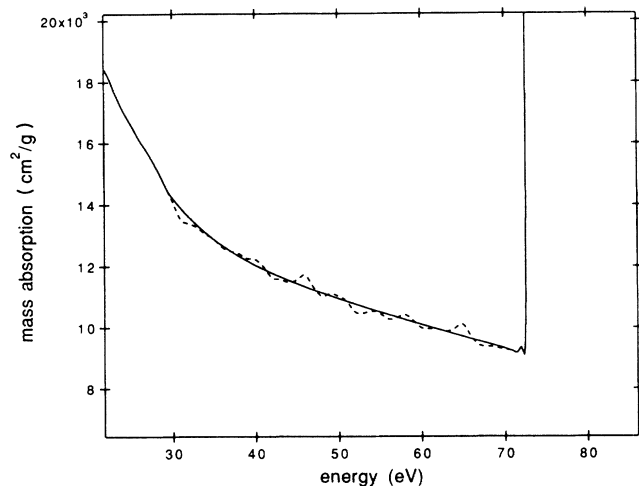$$\log_{10}\mu(\omega) = \sum_{i=0}^{4} A_i [\log_{10}(\omega)]^i .$$ (6)

FIG. 2. Aluminum mass absorption showing the modifications (solid line) made to the spectrum (dashed line) of Shiles and co-workers (Refs. 5 and 6) immediately below the $L_{\mathrm{II,III}}$ edge.
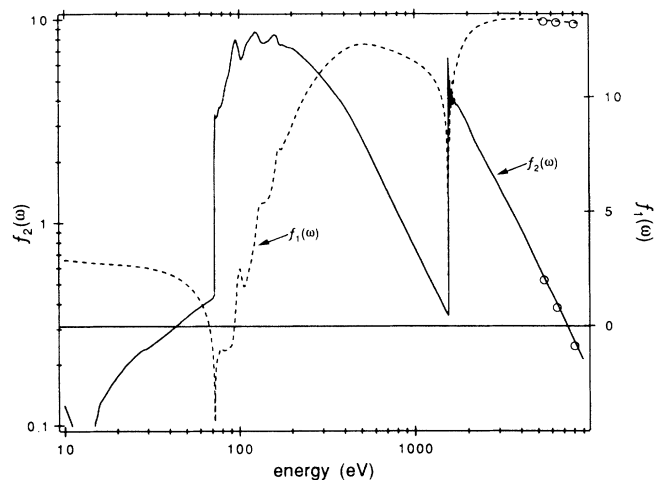

FIG. 3. The real (dashed line) and imaginary (solid line) parts of the forward-atomic-scattering factor of metallic aluminum compared with $f_1(\omega)$ and $f_2(\omega)$ from the theoretical values (open circles) of Cromer and Liberman (Ref. 38).

This smoothing changed $\mu(\omega)$ by less than 1% but removed all the anomalies in $f_1(\omega)$ between the K and L edges. This procedure was also applied to $\mu(\omega)$ from 30 to 70 eV. The results of the latter fitting compared with the original tabulation are shown in Fig. 2. The need for this correction was not apparent in the calculation of the refractive index, as done by Shiles et al.,[5] since $n \approx 1$ in this region.

V. RESULTS AND DISCUSSION

The most obvious difference between the present K-edge absorption spectrum and previous absorption data bases, is the prominent, broad peak at the core-excitation threshold energy. This peak is not apparent in all EXAFS studies[20,22,23] but is found in those that concentrated on the near-edge structure.[19,21,27,30,31] This unusual "white line" is quite broad compared to that of the $2p$-$3d$ autoionization lines seen in d-band metals. A simple explanation of this peak as an excitation to a localized final state is not possible since this peak is broader in energy than any absorption feature in the band structure above the Fermi level. The peak is not observed in the atomic state, but is seen in metallic aluminum and its oxide.[27] This absorption feature, which has been observed in other light elements,[33] is not predicted by the Mahan-Nozieres-de Dominicus theory[34] of the many-electron response to the creation of a core hole. Rather, it has been speculated[27,33] to arise from a continuum resonance similar to Fano or barrier resonances.[35]

Assuming the accuracy of our composite near-edge absorption data, we now consider the effect of this detailed spectrum on the forward-scattering factor (Fig. 3) especially near the K edge (Fig. 4) as calculated using Eq. (2). The EXAFS oscillations in $\mu(\omega)$ produce corresponding structure in $f_1(\omega)$ and there is a pronounced minimum in the scattering at the K-edge threshold energy.[36] The scattering factor evaluated at the edge from the modified absorption spectrum [$f_1(1560 \text{ eV})=1.9$] is substantially

smaller than that given by the Shiles data base [$f_1(1560 \text{ eV})=4.3$]. This difference arises from the large resonance peak that exists in the metallic aluminum absorption spectrum. One can see that the nature of the near-edge structure has a significant effect on the calculated forward-scattering factor.

It is instructive to compare the K-edge absorption of room-temperature metallic aluminum and the theoretical calculations of the photoionization cross section for the atomic species. Figure 5 shows the K-edge absorption from this work compared with the semiempirical absorption of Henke et al.[18] and with two theoretical calculations by Scofield.[32] These cross sections have been tabulated in a report by Saloman and Hubbell.[37] The two
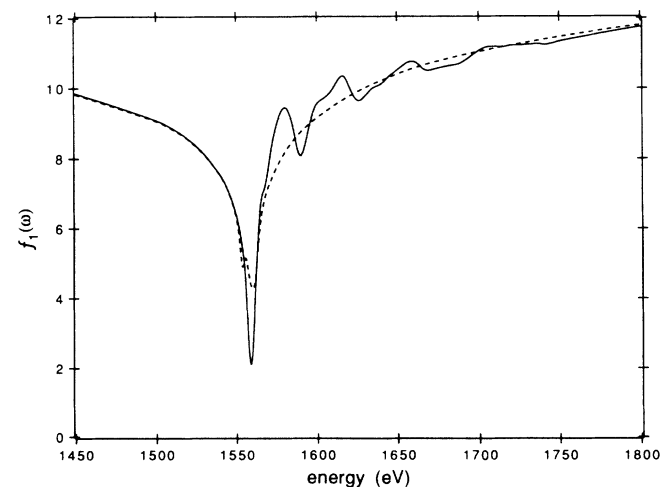

FIG. 4. The real part of the forward-scattering factor $f_1(\omega)$ at the aluminum K edge as a function of photon energy. The dashed curve is calculated from the absorption spectrum of Shiles and co-workers (Refs. 5 and 6) and the solid line is from the present work.
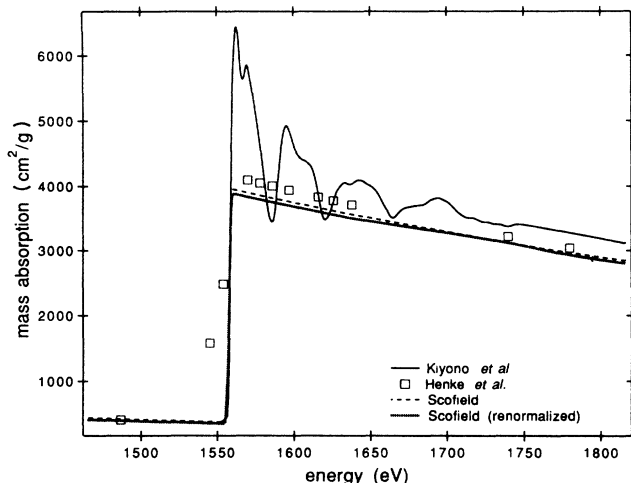
FIG. 5. K-edge absorption spectrum of metallic aluminum from this work (solid line) as compared with various tabulations of the absorption for the atomic species.

theoretical curves of Scofield were obtained from a relativistic calculation for electrons moving in a Hartree-Slater potential, and in a renormalized Hartree-Fock potential. One notes that there is little difference between Scofield's two calculations. This is to be expected since the two potentials are very nearly the same within the K shell. The Henke tabulation is similar to the relativistic calculations except near the edge, where it does not agree as well with Scofield's calculations. The preceding tabulations for the atomic species report a smaller absorption at the K edge than the absorption measured for the solid (Fig. 5). At energies sufficiently below and above the K edge, as one would expect, the atomic calculations join smoothly with the data for the condensed phase. At energies substantially above the aluminum K edge, Cromer and Liberman's theoretical determinations of the real and imaginary part of the scattering factor[38] agree with the results presented here to within 0.5%. Figure 3 compares $f_1(\omega)$ and $f_2(\omega)$ from this work as a function of energy from 10 to 10^4 eV with the Cromer and Liberman values[38] at the $K\alpha$ energies of common x-ray tube targets.

The energy loss of fast charged particles in aluminum can be determined from the dielectric-response function and compared to the results of electron-energy-loss measurements. A useful measure of the electron-energy-loss is the mean excitation energy[39] I given by

$$\ln I = \frac{\int_0^\infty \omega \mathrm{Im}[\epsilon^{-1}(\omega)]\ln(\hbar\omega)d\omega}{\int_0^\infty \omega \mathrm{Im}[\epsilon^{-1}(\omega)]d\omega} . \tag{7}$$

The present dielectric-function results in $I = 165$ eV, which is a reduction of 0.5 eV from the value of I calculated by Shiles et al.[5] This is well within the uncertainty of the best experimental value of 167 eV determined from energy-loss measurements.[5,40] An important point in calculating the mean excitation energy is that I, since it is weighted by a factor of ω, is more sensitive to changes in the K- and L-edge spectra than is the f sum.

VI. CONCLUSIONS

The present analysis of the scattering factors of aluminum, although using a well-established technique, points out some interesting features of the optical properties of aluminum and of metals in general. Older Kramers-Kronig calculations of metals are notorious for introducing error in the low-energy (Drude) extrapolation. This problem appears to have been resolved satisfactorily for aluminum.[5,6,16] The absorption spectrum of aluminum separates quite naturally into distinct contributions from different atomic subshells and the solid-state band structure, so that the previous analysis has virtually eliminated uncertainty in the global properties of the spectrum. Thus the error in the scattering factor derived from the present dispersion analysis depends mainly on the uncertainty of the experimental data from which the composite absorption spectrum is obtained. Seemingly small changes in $\mu(\omega)$ near absorption edges produce significant changes in the forward-scattering factor that can only be discussed in detail for aluminum because of the fairly complete knowledge of the optical properties of aluminum throughout the spectrum.

The substantial difference in scattering factor at the K edge between this work and previous compilations[5,6] should be measurable through direct techniques such as interferometry.[41] It would be useful to have these direct results to provide experimental verification of the theory and the techniques employed in this study, as well as to resolve remaining discrepancies in the x-ray optical constants of aluminum.

A tabulation of the real and imaginary parts of the scattering factor for aluminum along with its square amplitude and the optical constants from 20 to 10^4 eV is available from the authors. This tabulation has also been deposited with the American Institute of Physics Auxiliary Publication Service.[42]

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