X-Ray Mass Attenuation Coefficient of Silicon: Theory versus Experiment

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We compare new experimental x-ray total mass attenuation coefficients of silicon obtained with the x-ray extended-range technique (XERT) from 5 to 20 keV with theoretical calculations and earlier experimental measurements over a 5 to 50 keV energy range. The accuracy of between 0.27% and 0.5% of the XERT data allows us to probe alternate atomic and solid state wave function calculations and to test dominant scattering mechanisms. Discrepancies between experimental results and theoretical computations of the order of 5% are discussed in detail. No single theoretical computation is currently able to reproduce the experimental results over the entire 5 to 50 keV energy range investigated.

Structural determinations near absorption edges using synchrotron radiation sources, multiple-wavelength anomalous dispersion techniques, and x-ray absorption fine structure investigations have shown many successes in recent years. They provide information on local electron density distributions, lattice spacings, atomic environments in solids, and excited-state occupation levels.

However, the x-ray interaction away from edges can be just as revealing about the electronic structure, inner-shell orbitals, and relativistic corrections to atomic structure. Such measurements can critically probe the transform of the electron density as represented by the form factor, in a region where atomic theory (rather than solid state theory) dominates. The form factor describes photon-atom interactions and is therefore important in many fields of fundamental and applied physics. Hence the development of probes to critically test form factors will enhance our understanding of relativistic quantum mechanics and of fundamental atomic physics. If there are significant concerns and discrepancies far from any absorption edges, then drawing detailed conclusions in the complex region near edges should be carefully reevaluated.

Crystalline silicon is among the most perfect of crystalline materials whose lattice and structure have been characterized to the highest accuracy. Because of the importance of quality control in modern computer chip production, the link between atomic and macroscopic properties of silicon can be made to high accuracy. It is, therefore, often assumed that the atomic form factor and individual attenuation cross sections of silicon are also accurately known; but these are not more reliable than those of other elements.

Methods for determining atomic form factors include x-ray interferometry [1], reflection and refraction [2], diffraction intensities, and pendellösung fringes [3], with developing efforts at synchrotron facilities. These approaches are complemented by attenuation measurements which can determine the imaginary part of the

atomic form factor over an extended range of x-ray energies [4–6].

There has been a significant number of theoretical calculations of atomic form factors and detailed cluster calculations near x-ray absorption edges for solid state studies. At present, tabulations most widely used by different scientific communities are those of Scofield [7] and Saloman, Hubbell, and Scofield [8], Henke *et al.* [9,10], Creagh *et al.* [11], and Chantler [12,13]. These have raised numerous questions regarding the validity of details in the computation of form factors, including the nature of the correct relativistic corrections [14], the validity of dipole and multipole approaches [15], relativistic (Dirac-Hartree-Fock) versus nonrelativistic [Hartree-Slater (HS)] computations, unrenormalized versus renormalized HS results [7,16], modified versus unmodified form factor approaches [17], and the value of *S*-matrix formalisms [18].

Detailed comparisons of experimental results have been previously made with tabulations of Scofield, which exist in two forms. The first form (unrenormalized) is based on Hartree-Slater orbitals and hence omits certain relativistic corrections. This limitation would be expected to yield a lower accuracy than the self-consistent Dirac-Hartree-Fock approach. For $Z = 2$ to 54, Scofield provided estimated renormalization factors to convert to values which might be expected from a relativistic Hartree-Fock model. This correction was based primarily on the sum of component orbital electronic amplitudes at the nucleus and so is not equivalent to a fully relativistic procedure. The differences between renormalized and unrenormalized results vary from 5% to more than 15%.

Scofield's original recommendation to apply the renormalization correction in all cases should yield an improvement at high energies for all *Z*. A decade-long discussion has concerned itself with the relative validity of the renormalized and unrenormalized calculations of a Schrödinger versus Dirac approach. Some reviewers

found that this improved agreement with experiment [19]. Others concluded that unrenormalized results were superior [20] or that the experimental result lies between the renormalized and unrenormalized calculations [8,21,22]. The last statement would imply errors in the theoretical calculations of 5%–10%, as opposed to the claimed theoretical accuracy of 0.1%–1%. The statement has been questioned recently [23] using experimental data [24] which have, however, significant imprecision as seen from the inconsistency of adjacent data points. The unrenormalized version of Scofield's calculation appears less reliable than his renormalized version for silicon and above 25 keV overestimates the photoelectric component by several percent.

As contributions from different interaction processes dominate the total attenuation coefficient over different energy ranges, the discussion of discrepancies between theories should include all components over a large energy range. For silicon below 30 keV, the discrepancy in the (total) mass attenuation coefficients is due mainly to that of the photoelectric cross sections. Above 30 keV, alternative Rayleigh scattering predictions differ by 11% and alternate thermal-diffuse scattering (TDS) predictions differ by more than 15%. At 50 keV, alternative total attenuation coefficients differ by 3% or so.

The experimental setup for the x-ray extended-range technique (XERT) silicon measurements was similar to that in a copper measurement reported earlier [25]. Multiple specimens and repeated measurements optimize the statistics and permit the study of systematic contributions (harmonics, scattering, and detector linearity) which are impossible to quantify in measurements using a single specimen [25,26]. The final experimental accuracy from 0.27% to 0.5% and the large number of our experimental points over the 5–20 keV energy range allow critical investigations of the energy dependence of theoretical predictions.

Figure 1 is a plot of the percent discrepancy of the mass attenuation coefficients between the theoretical predictions of the nonrelativistic Hartree-Fock-Slater model of Scofield [7] used by Berger and Hubbell in XCOM [27], the relativistic multipole computation of Creagh et al. [11], and the experimental and theoretical synthesis of Henke et al. [10], all referred to the relativistic Dirac-Hartree-Fock calculation of Chantler [12] (zero line). Also plotted is the percent discrepancy between the mass attenuation coefficients from experiments [4,5,28–32] and the prediction of Ref. [12]. The theoretically calculated total attenuation coefficients include Compton and Rayleigh scattering coefficients. Reference [10] provides Compton and photoelectric coefficients, but not coherent scattering coefficients. Where necessary we have, therefore, used coefficients of Refs. [12] or [33] as detailed in the figure, to allow equitable comparison.
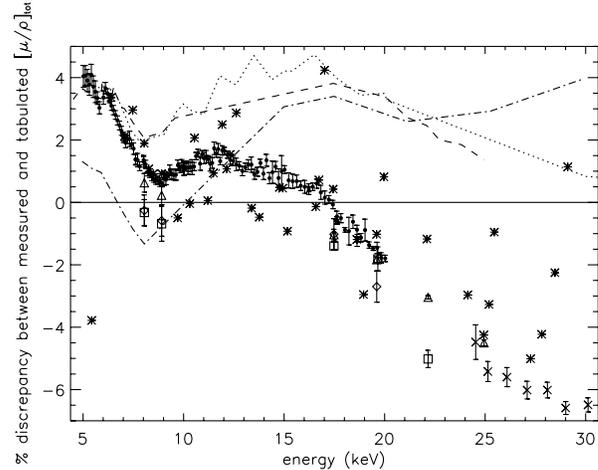

FIG. 1. Discrepancies in the total mass attenuation cross section of silicon between experiments from Gerward [30] ($\diamond$), Wang et al. [29] ($*$, error bars omitted for clarity), Creagh [4,28] ($\square$), Baltazar-Rodrigues et al. [31] ($\triangle$), Mika et al. [5] ($\times$), and this work ($\bullet$). Theoretical tabulations are presented from Chantler [12] (solid line), XCOM [27] [dotted line, Scofield [16] for photoelectric (PE), Hubbell et al. [33] for Compton and Rayleigh], Henke et al. [10] (dot-dashed line, Scofield [16] for Rayleigh), and Creagh [11] (dashed line). All theoretical curves are for amorphous silicon. Theoretical predictions of total cross sections are therefore the sum of PE, Compton, and Rayleigh components. At low energies scattering is minor but at higher energies all tabulations deviate from experiment due to the inadequacy of this scattering assumption. This is one of the first demonstrations of this type that Rayleigh scattering is invalid for perfect crystal silicon. The data of Wang have a large degree of imprecision. Predictions from the non-relativistic Hartree-Fock-Slater model (XCOM) are higher than those from the relativistic Dirac-Hartree-Fock (Chantler).

Experimental results of Wang et al. [29] quote 1%–2% error bars. However, the inconsistency at adjacent energy points and comparison with other data imply precision uncertainties of 2%–6% or up to 6 standard deviations of the quoted accuracy. The precision and accuracy of data from Ref. [29] is insufficient to discriminate between theoretical predictions, as is all low-energy data apart from our results. Data from Gerward [30] and from Baltazar-Rodrigues et al. [31] lie between the theoretical predictions. Experimental results of Creagh et al. [4] agree with Chantler except at Mo K_α. Excepting Mika et al. [5], other sources of experimental data (e.g., including [34]) are inconclusive in discriminating between tabulations due to the lack of experimental points, sufficient accuracy, or both.

It has been widely assumed that for crystalline materials coherent scattering is given by Laue-Bragg scattering or TDS. Coherent scattering in crystalline silicon may occur in an ideally anticorrelated manner yielding the TDS result. However, a reflection in the far wings of a Bragg peak (a misaligned orientation) can yield any

value between that of Rayleigh scattering and the TDS limit. The TDS assumption has until now not been confirmed by attenuation measurements while other measurements also yield a large uncertainty. The best previous attempt to confirm the thermal-diffuse nature of scattering in perfect crystal silicon using cross-section data was made by Creagh and Hubbell [4]. However, this was inconclusive experimentally, as the data presented agreed with one computation or scattering assumption in some regions, with another in other regions, and with none in further regions. More precise and extensive data were required.

Our experimental results together with those of Ref. [5] clearly show for the first time that all models assuming Rayleigh scattering for the coherent scattering component fail at the higher energies. These models correspond to an amorphous solid, whereas our silicon is a perfect crystal. One would therefore expect such tabulations to require the use of a more appropriate form for coherent scattering from near-perfect lattices, i.e., Laue-Bragg diffraction or a TDS cross section well away from Bragg peaks. The TDS cross section is much smaller than the Rayleigh cross section and brings the high-energy data into better agreement with theory, as seen in Fig. 2.

In the lower energy region of Fig. 2 the discrepancies of our measured mass attenuation coefficients are quite
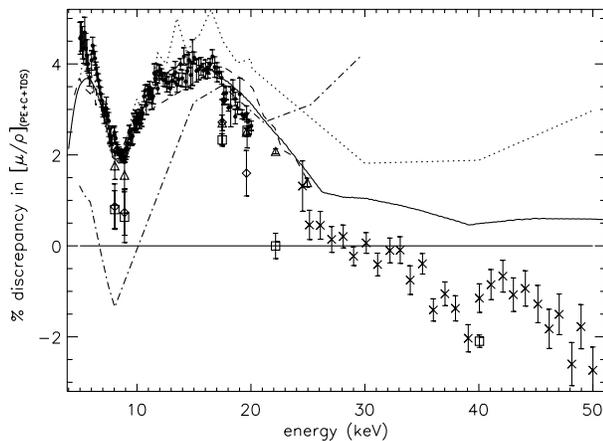

FIG. 2. Discrepancies in the total mass attenuation cross section of silicon between experiments from Gerward [30] ($\diamond$), Creagh [4,28] ($\square$), Baltazar-Rodrigues et al. [31] ($\triangle$), Mika et al. [5] ($\times$), and this work ($\bullet$). All theoretical curves are for ideally misaligned crystalline silicon. Theoretical predictions of total cross sections are therefore the sum of PE, Compton, and TDS components. Theoretical tabulations are presented from Chantler [12] (solid line), XCOM [27] (dotted line, Scofield [16] for PE, Hubbell et al. [33] for Compton, and Chantler for TDS), Henke et al. [10] (dot-dashed line, using Chantler for TDS), Creagh [11] (dashed line, using Chantler for TDS), and Kissel [35] (dot-dot-dot-dashed line, using Chantler for Compton and TDS). Agreement with theory is much improved.

close to Ref. [8] and reproduce structure in the discrepancy. But they are also fairly consistent with the relatively sparse set of theoretical points from [11], which is a relativistic multipole approach. As one approaches 20 keV, the discrepancy between our measured mass attenuation coefficients and [12] diminishes. Between 20 and 25 keV there is very little consistent experimental data. The trend of our data appears, however, to be picked up by Mika et al. [5] and between 25 and 33 keV these results are in very good agreement with Chantler's calculations [12]. Between 33 and 50 keV the data [5] fall below the zero line although the relative contributions of Compton and TDS scattering increase, reaching 50% and 25% of the photoelectric component at 50 keV. Hence a more critical assessment of the coherent and incoherent scattering coefficients is necessary to address discrepancies in this higher energy region.

The relative agreement of Refs. [7,8,11] in the lower energy range confirms that the relativistic effect is not significant at the level of 1% for silicon for energies lower than 20 keV. The relativistic correction does not appear to be the major factor responsible for the discrepancies between computations. It is perhaps surprising that Henke et al. [10] which use Refs. [7,8] as theoretical input, appear to be discrepant with that input data at all energies. This anomaly is explained by the authors [10]. Three theoretical predictions, tightly clustered around experimental results at 10 keV, begin to diverge between 11 and 17 keV. Up to about 19 keV the theory corresponding most closely with experiment is that of Ref. [35]. Interestingly this tabulation uses a Dirac-Slater approach and is quite similar to that of Refs. [7,8] also following the same trend. However, Ref. [35] diverges significantly from experimental data above this energy, to almost 3% discrepancy at high energies.

The observed increasing discrepancy between the theoretical prediction of Refs. [7,8,35] and the experimental data in the high-energy region (shown in Fig. 2) suggests an overestimation in the theoretical calculations of a combination of the photoelectric, Compton, and thermal-diffuse components. The difference between variously computed Rayleigh and thermal-diffuse scattering cross sections can have an appreciable influence on the comparison with nonrelativistic or relativistic theories, but all Rayleigh scattering models would impair agreement with experimental data. If scattering behavior is intermediate between Rayleigh and TDS computations, then comparison between experiment and theory becomes complex. Altering the magnitude of coherent scattering (TDS-like or otherwise) would shift the apparent energy at which a changeover occurs from the consistency of the experimental data with one theoretical tabulation [35] to that with an alternate theoretical tabulation [12]. It is clear that the crystal follows TDS-like behavior rather than Rayleigh scattering. Between 20 and 40 keV, the relativistic Dirac-Hartree-Fock approach [12] appears to

be in better agreement with the experimental data of Ref. [5]. Above 40 keV there is evidence that all tabulations overestimate at least one component of the total scattering process.

The behavior of the coherent scattering process (Rayleigh versus TDS) and the corresponding energy dependence could play an important role in addressing our residual discrepancy between theory and experiment. It may account for the changeover of the agreement with the two theories observed in Fig. 2. Electron correlation effects and the treatment of exchange correlation are also possible causes of the agreement of experimental data with one particular theory at low energies and another at higher energies. As these effects are strongly energy dependent, more sophisticated theoretical modeling of electron correlation and coupling are required to resolve this issue.

The experimental accuracy achieved by our use of the XERT is 1 order of magnitude better than the current discrepancies between theoretical computations and provides the first clear confirmation of TDS-like contributions in attenuation measurements using perfect crystal silicon. Moreover, it offers a detailed confirmation of the validity of approximations used in tabulations for silicon over medium x-ray energies. Further experiments and improvement in accuracy at energies between 20 and 30 keV, and above 40 keV, are strongly recommended to investigate this energy region in more detail, and to further probe the atomic wave functions.

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