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Resolution of a discrepancy of x-ray attenuation measurements of silicon in the energy range 25–50 keV

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Abstract. Precise measurements of the x-ray attenuation coefficient of crystalline silicon were made in the energy range 24 to 50 keV in 1985. As we show in this short paper, these measurements are of the highest precision currently available (1%–1.5%) for these energies. However, comparisons with theory were unable to resolve a residual discrepancy which reached seven standard deviations of the experimental precision over this range of energies. The most likely cause of the discrepancy was thought to lie in the estimation of the thermal diffuse scattering cross-section. We show that the dominant factor was, instead, the accuracy of the theory for the photoelectric component of the attenuation. Comparison with theory based on Chantler's work (Chantler C T 1995 *J. Phys. Chem. Ref. Data* **24** 71–643) shows agreement with experiment to within one standard deviation.

1. Introduction

A knowledge of x-ray attenuation coefficients is required in almost all fields in which the interaction of x-rays with matter is studied. The International Union of Crystallography (IUCr) instigated a project of attenuation measurements by different laboratories on standard samples, to assess and improve the reliability of published data. The final results of this project have been reported elsewhere (Creagh and Hubbell 1987, 1990) and are summarized for silicon, copper and graphite in the *International Tables for Crystallography* (Creagh and Hubbell 1992, Creagh and McAuley 1992). The best published data sets for these elements are those of Mika *et al* (1985) for medium-energy silicon and, independently, the earlier data of Gerward and Thuesen (1977).

These studies consisted of series of measurements of tuned and monochromated bremsstrahlung from fixed x-ray sources from 24 keV to 50 keV. In the later study 27 energies were used at roughly 1 keV intervals, with energy uncertainty of 20 eV, and the precision of the final results was approximately 0.5%. The authors concluded that the potential systematic error was less than 0.5%. In the former study, 18 energies were used across the same energy range, with an energy uncertainty from 40 eV to 200 eV, and an experimental uncertainty between 0.3% and 25%.

2. Comparison with theory

The comparison with theory included the photoelectric attenuation coefficient computed by interpolation from the data of Scofield (1973). Such interpolation is still widely employed

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as, for example, in Saloman *et al* (1988). The inelastic scattering coefficient was taken from Hubbell and Øverbø (1979) and Hubbell *et al* (1975). In both studies the thermal diffuse scattering (TDS) cross-section was determined following the procedure of Gerward and Thuesen (1977). The total attenuation coefficient μ_{TOT} is then given by the sum of three coefficients (in barns/atom) $\mu_{TOT} = \mu_{pe} + \mu_{TDS} + \mu_C$ where μ_{pe} is the photoelectric attenuation coefficient, μ_{TDS} is the contribution due to thermal diffuse scattering and μ_C is the contribution due to the Compton effect.

The earlier measurement (Gerward and Thuesen 1977) used the theory of photoelectric attenuation coefficients computed by interpolation from the data of Storm and Israel (1970), which is less commonly used today.

Theoretical approaches for the calculation of TDS contributions are largely equivalent. The use of Rayleigh scattering coefficients for pure crystalline silicon was expected to be incorrect since this assumes that scattering from each atom is incoherent with scattering from all others. The results proved the TDS approximation to be much more appropriate than the Rayleigh scattering estimate, since Rayleigh scattering would lead to larger theoretical cross-sections and hence to a greater discrepancy than is observed. There was no evidence for observation of constructive Bragg–Laue interference and scattering, which would have yielded an even greater discrepancy from experiment, and would have exhibited strong structure as a function of energy.

In the energy range investigated, the photoelectric attenuation coefficient is an order of magnitude larger than the inelastic (Compton) cross-section, which is larger again than the TDS cross-section.

Our comparison of the data of Mika *et al* (1985) yielded discrepancies which ranged from 1.1% at 24.53 keV (the lowest energy) to 3.5% at 50.01 keV (the highest energy) (figure 1). The discrepancy exhibited a clear and smooth trend, and a uniformly increasing offset. Our conclusion was that the precision of the measurements was originally correctly estimated at the 0.5%–0.6% level, but that a systematic error of up to 3.5%, or up to seven standard deviations

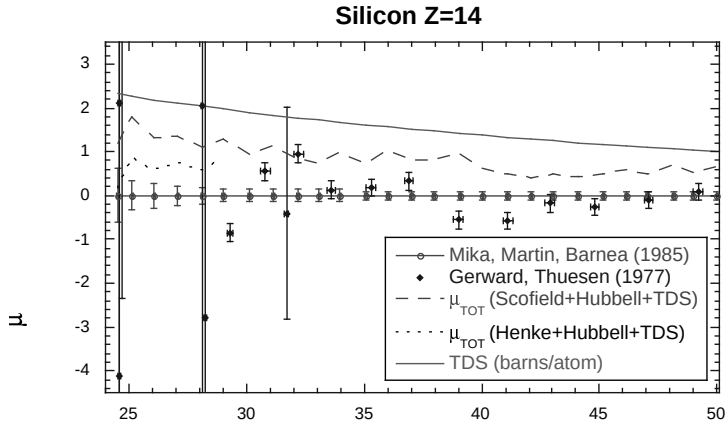

Figure 1. Comparison of the theory of Scofield (1973) and the experimental–theoretical synthesis of Henke *et al* (1988) with the experimental data of Mika *et al* (1985) and that of Gerward and Thuesen (1977). Results are plotted relative to the data of Mika *et al* (1985) as these represent the best experimental data set with the smallest quoted error bars. The total attenuation coefficient in barns/atom is computed as described in the text. The error bars are as stated in the experimental work. The contribution of thermal diffuse scattering is indicated on the same axis, for comparison.

of the experimental precision, would be required to explain the discrepancy.

At the time of the analysis, alternate theories for the contributions existed, and included that of Cromer and Liberman (1981); but these results were only available for discrete characteristic energies (e.g. Cu Kα or Mo Kα) and not for the continuum energies of the experiments. Hence they could not be applied to the data. It has taken several years to address noted deficiencies of alternative approaches with respect to their application to higher x-ray energies (Brennan and Cowan 1992, Chantler 1993).

3. Earlier conclusions

The first study (Gerward and Thuesen 1977) concluded that the theory of Storm and Israel (1970) was adequate to explain the data, but observation of the error bars shows that this was not the case. The conclusion of Mika *et al* (1985) that theory overestimated the attenuation coefficient is valid for both the Scofield theory (1973) and for the alternate use of Storm and Israel (1970).

Mika *et al* (1985) then logically concluded that the understanding of TDS was limited and that a 50% error of this theoretically computed contribution would explain the discrepancy. Hence further work on the role of TDS as an attenuation process was claimed to be necessary before more precise comparisons could be made.

4. New theory

The new theory of Chantler (1995) gives a probable resolution of this dilemma. This new result computes the photoelectric attenuation coefficient using fully relativistic DHF wavefunctions, and derives results for energies from below 1 keV to several hundreds of keV. For silicon across the energies of interest in this study, Chantler predicts a result lower than that of Scofield or Storm and Israel by about 1%. The results are plotted in figure 2. The difference between

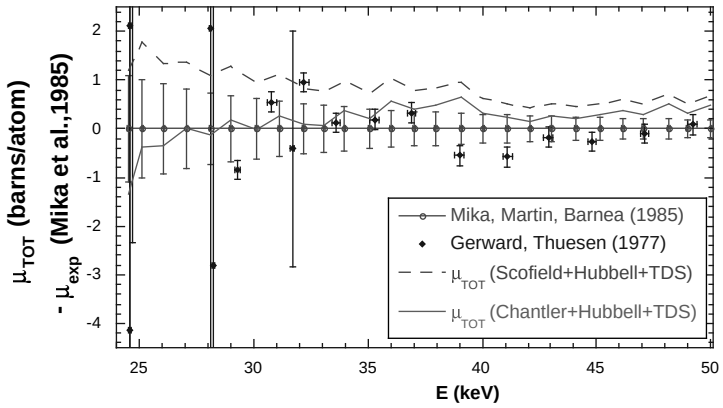

Figure 2. A plot of the theory of Chantler (1995) versus that of Mika *et al* (1985) for the same energy range. Results are again plotted relative to the data of Mika *et al* (1985). The experimental error includes estimated statistical and systematic errors. The results of Gerward and Thuesen (1977) are consistent with a precision of 1.5%. The results of Mika *et al* (1985) are consistent with a total uncertainty of 1%. The estimated accuracy of the new theory is better than 1%. There is a trend which suggests a residual systematic discrepancy between experiment and theory. Note that the apparent correlated noise of the two theories is actually due to fluctuations of the experimental data used to define the reference position.

the theory of Chantler and earlier theory in this case is largely due to the use of relativistic wavefunctions, and secondarily to the degree of convergence of the computation. On these grounds it would be expected that Chantler's theory is more reliable.

We assume in the comparison of figure 2 that the computations of inelastic scattering and of TDS are still valid, at least at the 10% level.

5. Resolution of the earlier discrepancy

The results of Gerward and Thuesen (1977) are consistent with a precision of 1.5%, or two to three times the statistical errors quoted. Moreover, this is consistent with the energy uncertainty of 200 eV, which would shift coefficients by 1.5% to 2% across the energy range investigated.

The results of Mika *et al* (1985) are consistent with a total uncertainty of 1%, as claimed in the original paper (i.e. a combination of the precision of 0.5% to 0.7% plus a systematic error of similar magnitude). The estimated accuracy of the new theory is better than 1%.

The conclusion regarding TDS is seen to be unfounded. In other words, it is likely that the computations of TDS were accurate at the 10% level and therefore did not contribute a major error in the result. The main error in previous comparisons was due to the use of inadequate theory concerning the dominant contribution to the attenuation measurement—the photoelectric absorption coefficient.

In addition to this conclusion, there is a trend which suggests a residual systematic error in experiment or theory, at below the 1% level. This systematic error could be due to details in the measurement and calibration, or in the theory of the photoelectric absorption, inelastic scattering, TDS, or in the simple approximation of a linear sum of coefficients in the final measurement. This residual discrepancy is rather small but very interesting. Given the limitation in accuracy represented by both calculations of theoretical contributions and experiment, the determination of the source of this systematic error will remain an interesting issue.

This systematic error changes sign with increasing energy, and will be the subject of new experiments in the near future.

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References

Brennan S and Cowan P L 1992 A suite of programs for calculating x-ray absorption, reflection, and diffraction performance for a variety of materials at arbitrary wavelengths *Rev. Sci. Instrum.* **63** 850–3

Chantler C T 1993 Improvements in computation of form factors *Radiat. Phys. Chem.* **41** 759–66

Chantler C T 1995 Theoretical form factor, attenuation, and scattering tabulation for $Z = 1$–92 from $E = 1$–10 eV to $E = 0.4$–1.0 MeV *J. Phys. Chem. Ref. Data* **24** 71–643

Creagh D C and Hubbell J H 1987 *Acta Crystallogr.* A **43** 102–12

Creagh D C and Hubbell J H 1990 *Acta Crystallogr.* A **46** 402–8

Creagh D C and Hubbell J H 1992 X-ray absorption (or attenuation) coefficients *International Tables for Crystallography* vol C, ed A J C Wilson (Dordrecht: Kluwer) section 4.2.4, pp 189–206

Creagh D C and McAuley W 1992 X-ray dispersion corrections *International Tables for Crystallography* vol C, ed A J C Wilson (Dordrecht: Kluwer) section 4.2.6, pp 206–22

Cromer D T and Liberman D A 1981 Anomalous dispersion calculations near to and on the long-wavelength side of an absorption edge *Acta Crystallogr.* A **37** 267–8

Gerward L and Thuesen G 1977 *Z. Naturf.* a **32** 588–93
Henke B L, Davis J C, Gullikson E C and Perera R C C 1988 *Lawrence Berkeley Laboratory Report* LBL-26259, UC-411
Hubbell J H and Øverbø I 1979 Relativistic atomic form factors and photon coherent scattering cross sections *J. Phys. Chem. Ref. Data* **8** 69–105
Hubbell J H, Veigele W J, Briggs E A, Brown R T, Cromer D T and Howerton R J 1975 Atomic form factors, incoherent scattering functions, and photon scattering cross sections *J. Phys. Chem. Ref. Data* **4** 471–538
Mika J F, Martin L J and Barnea Z 1985 *J. Phys. C: Solid State Phys.* **18** 5215–23
Saloman E B, Hubbell J H and Scofield J H 1988 X-ray attenuation cross sections for energies 100 eV to 100 keV and elements $Z = 1$ to $Z = 92$ *At. Data Nucl. Data Tables* **38** 1–197
Scofield J H 1973 *Lawrence Livermore National Laboratory Report* UCRI-51326
Storm E and Israel H I 1970 *Nucl. Data Tables* **A7** 565