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Estimates of X-ray Attenuation Coefficients for the Elements and Their Compounds

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Some recent developments leading to improved knowledge of the distribution of oscillator strength in the photo-ionization continua of atoms are briefly reviewed. Selective comparisons between the experiments and calculations are indicated. Estimates for attenuation by compounds and solids, insofar as they depart from the mixture rule, require an understanding of X-ray fine structure or, at least, of its limiting form, which is not yet at hand. Some of the mechanisms leading to fine structure in solids and molecules are briefly reviewed.

Introduction

There is an evident appeal in the use of those methods of obtaining attenuation corrections to intensity measurements from an analysis of reflection type measurements which are discussed by Milledge (1969) and Huber (1969) at this conference. As recently described (Kopfmann & Huber, 1968; North, Phillips & Scott Mathews, 1968) these methods progress from merely having a desirable objectivity to being essential in the study of those specimens which have to be handled while immersed in mother liquor. Even so, in other than the last mentioned extremity, something is usually known about sample size and shape; there thus still some interest in otherwise derived estimates of the attenuation coefficients. For some purposes, and in the case of specimens of well-controlled external morphology, it appears that correction for absorption independently estimated coefficients continues to be desirable.

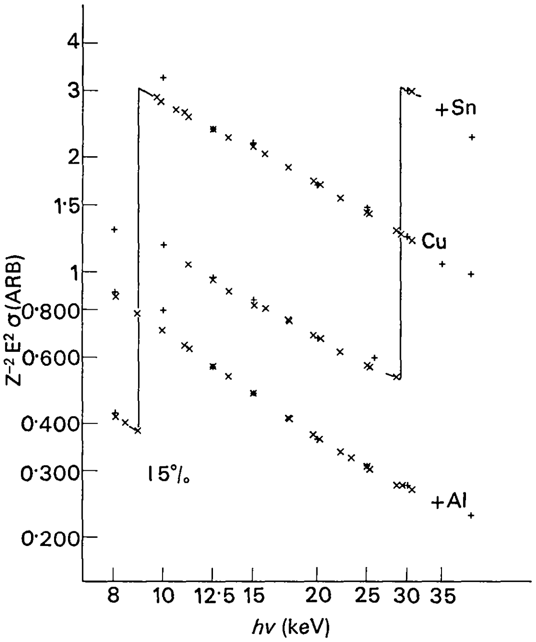

Fig. 1. A comparison of the results of measurements on total attenuation coefficients by A. J. Bearden, +, and the author, ×. The ordinate scale is 'reduced' by the indicated factors to permit display of small differences.

There are, of course, a number of problems intervening between satisfactory estimation of an attenuation coefficient and correction of an experimental intensity measurement using this information, *e.g.* Meulenaer & Tompa, (1965); Coppens, Meulenaer & Tompa (1967); Santoro & Zocchi (1967). I propose to ignore all of these problems largely in deference to their difficulty but also for the sake of finding a sufficiently restricted area of discourse. It is assumed, in particular, that there is available a procedure for utilizing 'good geometry' (collimated source, collimated detector) total attenuation coefficients to correct intensity measurements. The usual geometrical parameters of small single-crystal structural work suggest that the problems associated with 'too good' geometry (Parratt, Porteus, Schnopper & Watanabe, 1959) are not limiting here. I shall rather be concerned with estimates of attenuation coefficients for atoms and molecules isolated and in crystalline solids.

Although attenuation coefficients for use in crystallography are required only in a rather restricted wavelength region, activity outside that region offers several insights. Accordingly, I shall consider work both above and somewhat below the photon energy region of crystallographic interest. The past decade has seen progress in: (1) experimental determination of total attenuation coefficients mostly carried out on solid foils and rare gases; (2) theoretical estimates going beyond the hydrogen-like approximation for the (dominant) photoionization contribution to attenuation for free atoms. Within the first few hundred eV of an edge there is often significant fine structure in the solid attenuation spectrum; however, at energies more than a thousand eV above absorption edges, experiments on elemental solids tend to agree rather closely with calculations for gases. Although the fine structure in solids is not yet understood, certain aspects of recent atomic calculations are suggestive in this regard.

Attenuation in a polyatomic system, gaseous or otherwise, is less easily studied. The commonly used 'mixture rule' equates the absorption by a compound system to that of a stoichiometric mixture of its atomic constituents regardless of its state of aggregation. That this rule manifestly fails at least near absorption edges even in the gas phase suggests that its use for compound solids needs even more restraint. Again, in this case, certain features of the recent atomic calculations are suggestive of a basis for a consistent approach to this problem.

Experimental situation

It was somewhat more than ten years ago that the preparation of a survey of X-ray attenuation coefficients (White-Grodstein, 1957), brought into clear view our then rather poor knowledge of their values. It appeared that almost nowhere could one have confidence that the available information was good to even 10%. Apparent agreement between numbers appearing in various places could often be traced to their having come from the same source. The theoretical framework available was not significantly more satisfactory. In the energy region ($h\nu < 100$ keV), the photo-effect calculation was essentially hydrogenic with Slater screening numbers and with empirical correction later seen to have based on poor experimental data.

Several new measurement efforts were initiated at least partly in response to this situation. These various efforts all sought to improve experimental accuracy. Two among them claimed better than 1% in the final data (Bearden, 1966; Deslattes, 1959). A comparison of these results is suggestive of the present experimental situation. These were rather independent measurements with A. J. Bearden working in Baltimore while I was in Tallahassee. We used different samples, instruments, and techniques. In both cases, however, considerable efforts were applied to sample characterization.

For part of the region in which we overlap, I have indicated a comparison of our experimental results in Fig. 1. These data suggest that one or both of us had marginally significant systematic errors beyond those for which we so laboriously corrected. It is difficult to identify any one thing as a likely cause.

On the other hand, it is somewhat satisfying to note that these data and, for example, those of Cooper (1965) and of Middleton & Gazzara (1967) are generally in better agreement than earlier ones.

These data and many more are included in the survey prepared at Lawrence Radiation Laboratory (McMaster, Kerr-del Grande, Mallett, Scofield, Cahill & Hubbell, 1967, 1968). These workers have the entire experimental situation in computerized form. The data are weighted according to claimed accuracy or to estimates thereof by the compilers.

Their procedure has been to subtract theoretical scattering cross-sections from the experimental total cross-sections to obtain 'derived experimental' photoelectric cross-sections. The log-log images of these data were then subjected to a polynomial fit.

The results of this stage are presumably suitable for comparison with calculated photo-effect cross-sections. Adding these to the previously-subtracted theoretical scattering cross-sections should yield (somewhat reasonably) smoothed experimental data. Note that the likely errors in the scattering cross-sections do not, in the end, seriously affect the output totals.

Atomic calculations

The theoretical situation has made comparatively rapid progress in the last decade. Largely this has been made possible by the increased computing machine capability and its reduced cost. However, that is not to say that these results have been devoid of new insights. Rather, some of the results are susceptible of quite pretty interpretation and offer suggestions for approaches to polyatomic problems.

Quadrupole corrections to the cross-section have recently been discussed by Guttmann & Wagenfeld (1967) in the hydrogen-like approximation. Little in the way of chemical effects may be anticipated from this source, so its discussion will be omitted.

The first of the recent model calculations is due to Cooper (1962) who employed Hartree wave functions for the ground state and used a consistent potential in which to calculate numerical continuum solutions to the Schrödinger equation. Several effects appear in this calculation which are automatically excluded in hydrogenic calculation and in those using plane wave continuum states energy independent normalization.

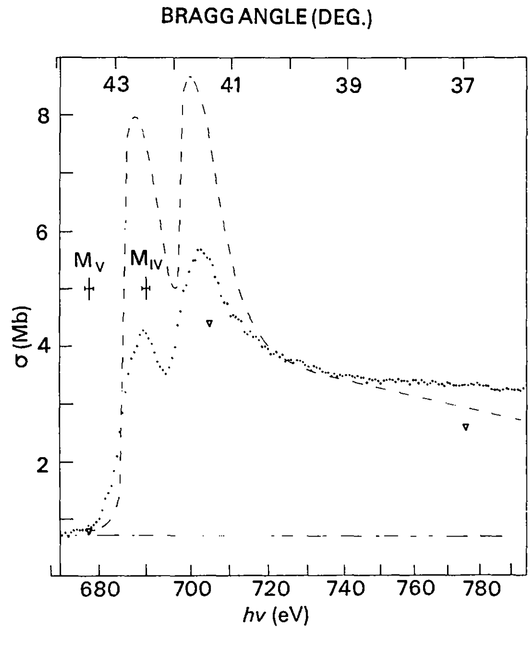

Fig. 2. Extremely non-hydrogenic behavior in xenon near the M_{IV} ($3d$) thresholds. The dashed line is theoretical, by courtesy of S. T. Manson (Manson & Cooper, 1968). Inverted triangles are from measurements with discrete lines (Lukirskii, Brytov & Gribovskii, 1965). The dots are the experimental results from a continuum source (Deslattes, 1968).

Recent extension of this work will be discussed somewhat later.

Machine solutions of the Dirac equation for a modified Fermi–Amaldi potential have been used by Rakavy & Ron (1967). The modification of the Fermi–Amaldi potential consisted in allowing explicitly, though rather approximately, for the presence of an inner hole when reckoning the final state (Shalatin, 1965). Extensive numerical results have been readily obtained from this work.

Pratt and his students have, in an extended series of papers, studied the effect of screening on the photoionization cross-section. Their emphasis has been on high photon energies; hence they have also used the Dirac equation, but in screened and unscreened Coulomb potentials. References may be found in the most recent of these papers (Schmickley & Pratt, 1967). One of the nicer results of this work has been the demonstration that the primary effect of screening is on the normalization of the bound state wave function. This leads to a scaling procedure for connecting Coulomb (analytical) cross-sections with more realistic ones. Although not specifically designed for the threshold region, the results tend to agree with experiment to remarkably low energies, often below twice threshold energies. They, of course, do not yield the specifically threshold effects such as those to which attention is now directed.

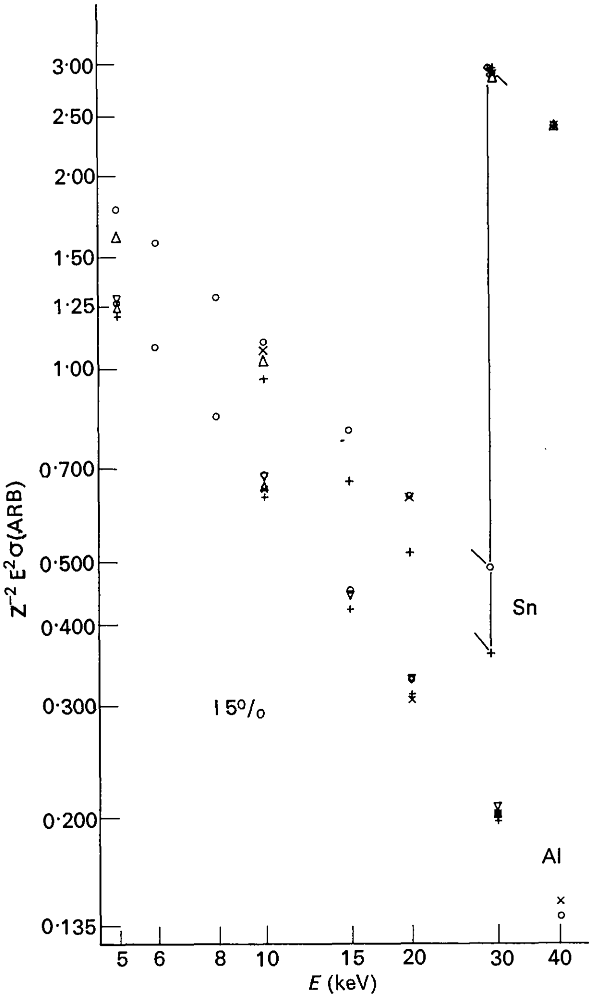

Fig. 3. Comparison of various calculations and 'experiments' for the reduced photoionization cross-section of Al and Sn. The 'experimental' points, ○, are derived from measured total attenuation coefficients by subtracting calculated scattering cross-section as employed in the most recent extensive concordance (McMaster *et al.*, 1967, 1968). Theoretical values from various sources are indicated as follows: +, hydrogenic, △, Rakavy & Ron, 1967; ×, Schmickley & Pratt, 1967; ▽, Manson & Cooper, 1968.

The most recent extension of the model calculation of Cooper (Manson & Cooper, 1968) has employed more realistic central potentials and covered a sufficient range of atomic numbers and photon energies to exhibit the Z dependence of certain threshold effects noted previously in isolated cases. As an example of what is found, the calculations suppress the thresholds for photoionization principally into a high angular momentum continuum. (Qualitatively, this represents a centrifugal barrier effect.) Thus the 'edge' is absent or much reduced in size. At higher energies, the cross-section rises above the level one might extrapolate to from higher energies. This situation as seen in the $3d$ region of xenon (Deslattes, 1968) is shown in Fig. 2. Related behavior has been noted in solid samples of Sn (Codling, Madden, Hunter, & Angel, 1966) and in the rare earths (Zimkina, Fomichev, Griboviskii & Zhukova, 1967). Further examples and a more general treatment may be found in a recent review article (Fano & Cooper, 1968).

Threshold effects aside, it is of interest to compare the most recent theoretical calculations with each other and with experiment. Since far more extensive comparisons of this sort will be available in the near future, I consider only two examples, namely, Al and Sn (Fig. 3). The comparisons suggest that, at the one per cent level, alternative potentials and, in this energy range, the Dirac and Schrödinger equations are indistinguishable by the indicated experimental data for Al but are distinguished by the data on Sn. The comparison is based on subtraction of calculated scattering cross-sections (which are uncertain at present) from the experimental total cross-sections. The sizes of expected errors in scattering cross-sections are not significant at this error level. The overall situation is satisfactory from an empirical point of view. On the other hand, it is clear that the experiments do not always distinguish between different schemes.

Molecular gases and compound solids

Before getting to this subject directly, is it well to emphasize at least one of the limitations of the discussions up to now. The mono-atomic solid, or the homonuclear diatomic molecular gas, has a rich and often extended fine structure region to which the atomic calculations are not applicable. The K region of Al shown in Fig. 4 probably represents somewhat more structure than would be found in elemental solids in the region where crystallographic measurements are normally carried out.

The diatomic molecule also exhibits an extended fine structure (Sagawa *et al.*, 1968). At least in part, this may be seen to arise from a description of the photoionization process which takes account of the fact that the identity of the photo electron course is not specified by the experiment, hence the classically distinct processes interfere (Cohen & Fano, 1966). This description appears to be equivalent to the use of properly anti-symmetrized molecular orbitals for both the initial and final states for the photoionization process. A proper description of photoionization in a solid should include this type of 'unspecifiable source' interference. In this case, a mere use of Bloch wave functions probably does not cover all relevant problems. In these situations the 'mixture rule' would naturally assert the identity of atomic and aggregate cross-section when reckoned on a per atom basis.

Passing to the next simplest case, namely, that of the heteronuclear diatomic molecule removes the 'unspecifiable source' mechanism for violating the mixture rule. Nevertheless, fine structure is expected due to scattering of the photoelectron wave function by the partner potential. This scattering leads to a type of interference which forms the basis for most theoretical descriptions of absorption fine structure (Kronig, 1932; Corsen, 1946; Shiraiwa, Ishimura & Sawada, 1958; Koslenkov, 1961). The mechanisms envisaged here are probably not already accounted for in the above description of the photoionization of homonuclear diatomic molecules and elemental solids. Hence, one must expect to have to augment the former discussions in some way to take account of the potential external to the photo emitting atom.

There is a considerable formal resemblance between such scattering models and the beginning of a perturbation expansion of the Green's function solution to the positive energy Schrödinger problem. It is tempting to suspect that such successes as have been noted for these models derive from this analogy. In this case, any other, perhaps more tractable method, for obtaining the continuum function is equally acceptable.

One might envision a program carried out for molecules in analogy to one of the recent atomic calculations, for example, that of Cooper (1962). The essential elements would be use of a relatively decent wave function for the inner state and a numerical solution for the continuum function in as consistent a model potential as is feasible. By analogy with the atomic calculation, one may expect that the dominant effect of the external structure of the potential will be, *via* the normalization condition, on the amplitude of the continuum function near the nucleus. The modulation of the square of this amplitude (to which the cross-section is proportional) as a function of photoelectron energy would be the dominant cause of fine structure.

Turning finally to some speculations regarding how one might proceed in the case of solids, recent work on the LEED problem (Marcus & Jepsen, 1968) suggests a mode of attack which has not yet been applied to the problem of X-ray fine structure. Marcus & Jepsen have approached the electron diffraction problem by coupling external and internal (Bloch) solutions of the wave equation by matching at a planar boundary between crystal and vacuum. In the X-ray case one might start with the interior of a particular Wigner-Seitz cell which has been singled out by removal of an inner shell electron. By analogy with the above electron diffraction calculation, matching could be attempted at the surface of the Wigner-Seitz cell, coupling interior type conti-

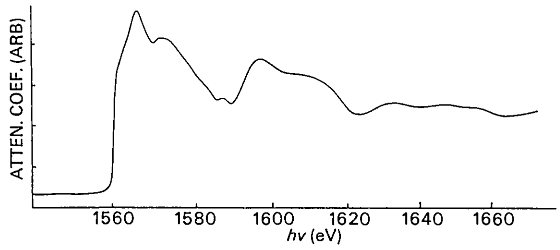

Fig. 4. The region above the K absorption threshold of Al for a metallic specimen.

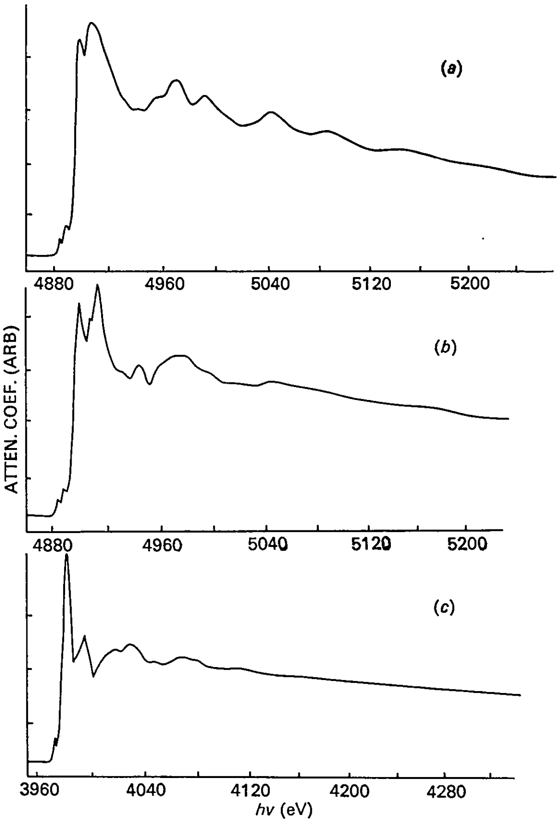

Fig. 5. The K series absorption fine structure of Ti in $SrTiO_3$ (*a*) and $CaTiO_3$ (*b*), and of Ca in $CaTiO_3$ (*c*).

nuum functions with both damped and undamped solutions throughout the rest of the crystal. Once again application of the normalization condition to the above solution would result in energy dependence of the square of the amplitude of the continuum function near the nucleus and thereby the cross-section.

Let me conclude by returning to one aspect of the empirical situation. About a year ago, J. Perel working in my laboratory completed an extensive set of measurements on a number of ABO_3 compounds which have the perovskite structure. Based on the then available simplified models of X-ray fine structure (but not on the hypothetical procedure noted above), we would have expected either to find various regularities or similarities in the spectrum of A while B was varied, or to find the spectra of A and B in the same system. None of these are evident in the data. Fig. 5 shows an example of the kind of results Perel obtained. What is evident from this example and from the remainder of the data is that quite radical changes in the long range fine structure occur for relatively modest changes in chemistry. This suggests that one must indeed consider the details of the crystal potential in attempting to understand the fine structure.

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DISCUSSION

ABRAHAMS: In view of the fine structure near an absorption edge, how many volts from that edge should one work, in order to reduce error in the additivity relation to less than 1 or 2 percent?

DESLATTES: 1000 volts is a reasonably safe figure. Some compounds of the ABO_3 type exhibit no fine structure.

WEISS: Our own experience is that if you require to know the absorption coefficient to better than 10% then do not rely on the values in the *International Tables*. It is then best to make up your own sample and determine the value experimentally.

MILLEDGE: In preparing the values for the *International Tables*, we decided to put the less reliable in italics – perhaps we should have put them all in italics. The trouble was that there just were not enough experimental values. Fortunately micro-probe techniques also require this information and we will gain indirectly from their activity.

WEISS: I doubt whether one can calculate the absorption coefficient to as good as 2%.

HAMILTON: The supplements to the *International Tables*, Volumes II and III, due probably in 1969, will contain improved values for the absorption coefficients.