

4.2. X-RAYS

current, and rather different, approach can be compared. Although a detailed comparison of the historical databases may be of some interest, the result would have only very small influence on the outcome presented here. To specify this framework, we begin with a brief description of the procedures used in establishing this reference database.

Bearden and his collaborators remeasured a group of five X-ray lines (Bearden, Henins, Marzolf, Sauder & Thomsen, 1964), with the remaining entries in the wavelength table coming from a critically reviewed, and re-scaled, subset of earlier measurements (Bearden, 1967). Line locations were given in \AA^* units, a scale defined by setting the wavelength of $W K\alpha_1 = 0.2090100\text{\AA}^*$. It was Bearden's intention that, for all but the most demanding applications, one could simply assign $\text{\AA}^*/\text{\AA} = 1$, with an uncertainty arising from the fundamental physical constants, particularly N_A and hc/e , combined with uncertainties arising from the measurement technology (Bearden, 1965). Not long after the publication of the final compilation (Bearden, 1967), it became clear that the fundamental constants used in defining \AA^* needed significant revision (Cohen & Taylor, 1973), and that there were some inconsistencies in the metrology (Kessler, Deslattes & Henins, 1979).

4.2.2.2. *Known problems*

Aside from the particular issues noted above, all previous wavelength tables had certain limitations arising from the procedures used in their generation. In particular, except for a small group of five $K\alpha$ spectra (Bearden, Thomsen *et al.*, 1964), the Bearden tables relied entirely on data previously reported in the literature. Both of the other tabulations also proceeded using only reported experimental values (Cauchois & Hulubei, 1947; Cauchois & Senemaud, 1978). In the Bearden compilation process, available data for each emission line were weighted according to claimed uncertainties, modified in certain cases by Bearden's detailed knowledge of the measurement practices of the major sources of experimental wavelength values. The complete documentation of this remarkable undertaking is, unfortunately, not widely accessible. Our evident need to understand the origin of the 'recommended' values has been greatly aided by the availability of a copy of the full documentation (Bearden, Thomsen *et al.*, 1964).

The actual experimental data array from which the previous tables emerged is not complete, even for the prominent ('diagram') lines. In the cases where experimental data were not available [as can be seen only in the source documentation (Bearden, Thomsen *et al.*, 1964)], the gaps were filled by interpolated values based on measurements available from nearby elements, plotted on a modified Moseley diagram in which the Z^2 term dependence is taken into account (Burr, 1996). In the end, such a smooth scaling with respect to nuclear charge suppresses the effects of the atomic shell structure, a practice that must be avoided in order to obtain the significant improvement in the database that we hope to provide. Also obscured in smooth Z scaling are detectable contributions arising from the fact that nuclear sizes do not change smoothly as a function of the nuclear charge, Z .

4.2.2.3. *Alternative strategies*

There are several possible approaches to generating an improved, 'all- Z ' table of X-ray wavelengths. These range from the option of conducting a massive measurement campaign to populate more fully the currently available tabular array to a large computational endeavor that might purport to carry out multiconfiguration, relativistic wavefunction calculations for the

entire Periodic Table. It seems evident to us that there is little interest in, and even less support for, mounting the large effort needed to realize an improved tabulation of X-ray wavelengths by purely experimental means, while the possibility of proceeding in an entirely theoretical mode is not consistent with the evident need that at least some wavelengths be reported with uncertainties that approach the limit of what can be obtained from the naturally occurring X-ray lines. The actual location of any useful feature of a line is influenced not only by the physical and chemical environment of the emitting atom but also by inevitable multi-electron excitation processes that perturb the entire spectral profile. Calculation of such complexities currently lies beyond the limits of practicality, eliminating the option of proceeding without strong coupling to experimental profile locations, at least for crystallographically important X-ray lines. Similar considerations apply *a fortiori* to those lines needed as reference wavelengths for exotic atom measurements, such as those leading to masses of elementary particles and tests of basic theory [see *e.g.* Beyer, Indelicato, Finlayson, Liesen & Deslattes (1991)].

In constructing the accompanying tables, we have chosen a new procedure that differs from those described above, and accordingly requires some detailed commentary. We begin with the presently available network of well documented experimental measurements, originally established to provide a test bed for the theoretical methods developing at that time (Deslattes & Kessler, 1985). This modest network was the first compilation to make use of the, then newly available, connection between the X-ray region and the base unit of the International System of measurement (the SI) based on optical interferometric measurement of a lattice period as revealed by X-ray interferometry. Details of the generation of this network and its subsequent expansion will be given below. Using this network as a test set gave clearer suggestions as to specific limitations of the theoretical modelling than had been evident from using other, less selective, experimental reference compilations available at that time. Extensive theoretical developments before and, especially, after the appearance of this new experimental reference set have shown a steady convergence toward these critically evaluated data. Following this evolution further, our long-term plan is to use these new theoretical calculations to provide a more structured and accurate interpolation procedure for estimating the spectra of elements lying between those for which we have accurate measurements, or spectra well connected to a directly established reference wavelength. The present table provides experimental and theoretical values for some of the more prominent K and L series lines and is a subset of a larger effort for all K and L series lines connecting the $n = 1$ to $n = 4$ shells. The more complete table will be published elsewhere and be made available on the the NIST Physical Reference Data web site. In addition, experimental values for the K and L edges are provided. Although the reference data are inadequate in both low and high ranges of Z , the general consistency of theory and experiment through the region $20 < Z < 90$ for the strong K -series and L -series lines suggests that, in the absence of good reference measurements, the uncorrected theoretical values should be considered for applications not requiring the highest accuracy.

4.2.2.4. *The X-ray wavelength scales, old and new*

Historically, from the first realizations of refined spectroscopy in the X-ray region (*ca* 1915–1925) up to the period 1975–1985, the best measured X-ray wavelengths had to be expressed in some local unit, most often designated as the xu (x unit) or kxu

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(kilo x unit). Uncertainty in the conversion factor between the X-ray and optical scales was the dominant contributor to the total uncertainties in the wavelength values of the sharper X-ray emission lines, such as those most frequently used in crystallography. (For a discussion of the present values in relation to previously assigned numerical values on the various scales, see Subsection 4.2.2.14.) This local unit was, for most of the time, 'officially' defined by assigning a specific numerical value to the lattice period of a particular reflection from 'the purest instance' of a particular crystal. Originally this was rock salt; later it was calcite. In practice, most work used as *de facto* standards certain values for Cu $K\alpha_1$ and Mo $K\alpha_1$ whose inconsistency, though noted by some crystallographers earlier, was seriously addressed by Bearden and co-workers only in the 1960's (Bearden, Henins *et al.*, 1964). This early history was summarized in 1968 (Thomsen & Burr, 1968). Connection of the X-ray wavelength scale to the primary realizations of the length (wavelength) unit in the 'metric system' was primarily (at least after about 1930) through ruled grating measurements of longer-wavelength X-ray lines such as Al $K\alpha_{1,2}$.

The remainder of the X-ray wavelength database was derived from relative measurements using crystal diffraction spectroscopy. Unfortunately, even the most refined among the ruled grating measurements did not give accuracies comparable to the precision accessible by relative wavelength measurements (Henins, 1971). As noted above, in connection with establishing the previous wavelength table, Bearden introduced a new local unit, the Å*, based on an explicit value for the wavelength of W $K\alpha_1$, chosen to give a conversion factor near unity. This transitional period will not be treated further in the present documentation since, to a substantial extent, developments described in the following paragraphs have effectively eliminated the need for a local scale for X-ray wavelength metrology.

Following the demonstration of crystal lattice interferometry in the X-ray region (Bonse & Hart, 1965), efforts to combine such an X-ray interferometer with various optical interferometers were undertaken in several (mostly national standards) laboratories. Although the earliest of these, carried out at the National Bureau of Standards (NBS) (now the National Institute of Standards and Technology, NIST) (Deslattes & Henins, 1973) was, in the end, found to be burdened by a serious systematic error (1.8×10^{-6}) in later work at the Physikalisch Technische Bundesanstalt (PTB) (Becker *et al.*, 1981; Becker, Seyfried & Siegert, 1982), it was clear that accuracy limitations associated with ruled grating measurements no longer dominated the metrology of X-ray wavelengths. The origin of the systematic error in the early NBS measurement was subsequently understood (Deslattes, Tanaka, Greene, Henins & Kessler, 1987), and, more recently, excellent results were obtained in Italy (Basile, Bergamin, Cavagnero, Mana, Vittone & Zosi, 1994, 1995) and Japan (Fujimoto, Fujii, Tanaka & Nakayama, 1997). In all cases, the goal was to obtain an optical measurement of a crystal lattice period (thus far, only Si 220) and to use the calibrated crystals in diffraction spectrometry to establish optically based X-ray wavelengths. Such exercises have been undertaken for several X-ray lines, but the most detailed and well documented results to date were obtained in Jena (Härtwig, Hölzer, Wolf & Förster, 1993; Hölzer, Fritsch, Deutsch, Härtwig & Förster, 1997), where the $K\alpha$ and $K\beta$ spectra of the elements Cr to Cu were evaluated using silicon crystals well connected with the crystal spacings measured at the PTB.

4.2.2.5. *K-series reference wavelengths*

In addition to the Jena measurements noted above, a number of characteristic X-ray lines were measured on the optically

based scale at NBS/NIST. The set of directly measured reference wavelengths is given in Table 4.2.2.1 in bold type. Most of the originally published (NBS/NIST) values were burdened by the 1.8×10^{-6} error in the silicon lattice period, as noted above. These have been corrected in the numerical results summarized in the table. The directly measured elements and lines appearing in this table were often chosen to meet the need for specific reference values in locations near those of certain optical transitions in highly charged ion spectra or spectra from pionic atoms. In addition, early NBS measurements specifically addressed the lines most often used in crystallography and the W $K\alpha$ transition. In response to the needs of electron spectroscopy, Al and Mg K spectra were also determined (Schweppe, Deslattes, Mooney & Powell, 1994). In this case, the original lattice error had been previously recognized, so that no rescaling was required. The remaining directly measured entries were obtained as opportunities to do so emerged.

The optically based data set was expanded by noting that several groups of accurate (relative) measurements in the literature either contained one of the directly measured lines (bold type) in Table 4.2.2.1 or were explicitly connected to one of them. Most often this situation was realized in reports that indicated a specific reference value, *i.e.* where it was stated numerical values are based on a scale where, for example, the wavelength of Mo $K\alpha_1$ was taken as 707.831 xu. In such cases, and where other indicators of good measurement quality are presented, it is easy to re-scale the data reported so that it is consistent with the optically based data. This procedure was followed for important groups of measurements from earlier work by Bearden and co-workers, and from the X-ray laboratory at Uppsala. The rescaled numerical results are included in Table 4.2.2.1 in normal type along with the specific literature citations. The indicated uncertainties are standard uncertainties as defined by ISO (Taylor & Kuyatt, 1994; Schwarzenbach, Abrahams, Flack, Prince & Wilson, 1995).

4.2.2.6. *L-series reference wavelengths*

To date, only a very limited number of *L*-series emission lines have been directly measured on an optically based scale. Wavelengths for directly measured *L*-series lines are reported in Table 4.2.2.2 along with the literature citations. In the future, we hope to expand this limited data set by including other lines and elements that are well connected to these reference lines in the literature.

4.2.2.7. *Absorption-edge locations*

Only a small number of absorption-edge locations have been directly measured to high accuracy using the currently acceptable protocols. Some of the available data were obtained in order to provide wavelength determinations for spectra from highly charged and/or exotic atoms (Bearden, 1960; Lum *et al.*, 1981). This small group was, however, significantly expanded very recently by an important set of new measurements, extending to $Z = 51$, that are well coupled to the optical wavelength scale (Kraft, Stümpel, Becker & Kuetgens, 1996). The resulting experimental database is summarized in Table 4.2.2.3. The effort that would be needed to expand the experimental database in a systematic way is quite large. Thus, we make use of a procedure, not previously used for this purpose, that combines available electron binding energy data with emission-line locations from our expanded reference set of emission-line data and emission lines that have been rescaled to be consistent with the optically based scale. At the same time, calculation of the location of absorption thresholds within the