

## 4. PRODUCTION AND PROPERTIES OF RADIATIONS

(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 rocksalt; 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 ( $1.8 \times 10^{-6}$ ) 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  $1.8 \times 10^{-6}$  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

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Table 4.2.2.1. *K-series reference wavelengths in Å; bold numbers indicate a directly measured line*

Numbers in parentheses are standard uncertainties in the least-significant figures.

Z	Symbol	A	$K\alpha_2$	$K\alpha_1$	$K\beta_3$	$K\beta_1$	References
12	Mg		<b>9.89153 (10)</b>	<b>9.889554 (88)</b>			(a)
13	Al		<b>8.341831 (58)</b>	<b>8.339514 (58)</b>			(a)
14	Si		<b>7.12801 (14)</b>	<b>7.125588 (78)</b>			(b)
16	S		<b>5.374960 (89)</b>	<b>5.372200 (78)</b>			(b)
17	Cl		<b>4.730693 (71)</b>	<b>4.727818 (71)</b>			(b)
18	Ar		<b>4.194939 (23)</b>	<b>4.191938 (23)</b>			(c)
19	K		<b>3.7443932 (68)</b>	<b>3.7412838 (56)</b>			(d)
24	Cr		<b>2.2936510 (30)</b>	<b>2.2897260 (30)</b>	<b>2.0848810 (40)</b>	<b>2.0848810 (40)</b>	(e)
25	Mn		<b>2.1058220 (30)</b>	<b>2.1018540 (30)</b>	<b>1.9102160 (40)</b>	<b>1.9102160 (40)</b>	(e)
26	Fe		<b>1.9399730 (30)</b>	<b>1.9360410 (30)</b>	<b>1.7566040 (40)</b>	<b>1.7566040 (40)</b>	(e)
27	Co		<b>1.7928350 (10)</b>	<b>1.7889960 (10)</b>	<b>1.6208260 (30)</b>	<b>1.6208260 (30)</b>	(e)
28	Ni		<b>1.6617560 (10)</b>	<b>1.6579300 (10)</b>	<b>1.5001520 (30)</b>	<b>1.5001520 (30)</b>	(e)
29	Cu		<b>1.54442740 (50)</b>	<b>1.54059290 (50)</b>	<b>1.3922340 (60)</b>	<b>1.3922340 (60)</b>	(e)
31	Ga		<b>1.3440260 (40)</b>	<b>1.3401270 (96)</b>	1.208390 (75)	1.207930 (34)	(b),(f)
33	As		<b>1.108830 (31)</b>	<b>1.104780 (12)</b>	0.992689 (79)	0.992189 (53)	(b),(f)
34	Se		1.043836 (30)	<b>1.039756 (30)</b>	0.933284 (74)	0.932804 (30)	(b),(f)
36	Kr		<b>0.9843590 (44)</b>	<b>0.9802670 (40)</b>	<b>0.8790110 (70)</b>	<b>0.8785220 (50)</b>	(b)
40	Zr		<b>0.7901790 (25)</b>	<b>0.7859579 (27)</b>	<b>0.7023554 (30)</b>	<b>0.7018008 (30)</b>	(b)
42	Mo		0.713607 (12)	<b>0.70931715 (41)</b>	0.632887 (13)	0.632303 (13)	(d),(f)
44	Ru		0.6474205 (61)	0.6430994 (61)	0.5730816 (42)	0.5724966 (42)	(d),(f)
45	Rh		0.6176458 (61)	0.6132937 (61)	0.5462139 (42)	0.5456189 (42)	(d),(f)
46	Pd		0.5898351 (60)	0.5854639 (46)	0.5211363 (41)	0.5205333 (41)	(d),(f)
47	Ag		<b>0.5638131 (26)</b>	<b>0.55942178 (76)</b>	0.4976977 (60)	0.4970817 (60)	(d),(f)
48	Cd		0.5394358 (46)	0.5350147 (46)	0.4757401 (71)	0.4751181 (71)	(d),(f)
49	In		0.5165572 (60)	0.5121251 (46)	0.4551966 (41)	0.4545616 (41)	(d),(f)
50	Sn		0.4950646 (46)	0.4906115 (46)	0.4358821 (51)	0.4352421 (51)	(d),(f)
51	Sb		0.4748391 (45)	0.4703700 (45)	0.4177477 (41)	0.4170966 (31)	(d),(f)
54	Xe		<b>0.42088103 (71)</b>	<b>0.4163508 (14)</b>	<b>0.3694051 (13)</b>	<b>0.3687346 (13)</b>	(d)
56	Ba		<b>0.38968378 (74)</b>	<b>0.38512464 (84)</b>	<b>0.3415228 (11)</b>	<b>0.34082708 (75)</b>	(d)
60	Nd		<b>0.3248079 (59)</b>	<b>0.3201648 (59)</b>	0.283634 (59)	0.282904 (44)	(d),(f)
62	Sm		<b>0.31369830 (79)</b>	<b>0.30904506 (46)</b>	0.273764 (30)	0.273014 (30)	(d),(f)
67	Ho		0.26549088 (84)	0.2607608 (42)	0.230834 (30)	0.230124 (30)	(f),(g)
68	Er		<b>0.2571133 (11)</b>	<b>0.25237359 (62)</b>	<b>0.2234766 (14)</b>	<b>0.22269866 (72)</b>	(d)
69	Tm		0.24910095 (61)	0.24434486 (44)	0.216366 (30)	0.21559182 (57)	(f),(h)
74	W		0.21383304 (50)	<b>0.20901314 (18)</b>	0.18518317 (70)	0.1843768 (30)	(d),(f)
79	Au		<b>0.18507664 (61)</b>	<b>0.18019780 (47)</b>	<b>0.1598249 (13)</b>	<b>0.15899527 (77)</b>	(d)
82	Pb		<b>0.17029527 (56)</b>	<b>0.16537816 (38)</b>	<b>0.1468129 (10)</b>	<b>0.14596836 (58)</b>	(d)
83	Bi		0.1657183 (20)	0.1607903 (46)	0.142780 (11)	0.1419492 (54)	(f),(g)
90	Th	230	<b>0.13782600 (31)</b>	<b>0.13282021 (36)</b>	<b>0.11828686 (78)</b>	<b>0.11740759 (59)</b>	(d)
91	Pa	231	0.1343516 (29)	0.1293302 (27)	0.1152427 (21)	0.1143583 (21)	(i)
92	U	238	<b>0.13099111 (78)</b>	<b>0.12595977 (36)</b>	<b>0.11228858 (66)</b>	<b>0.11140132 (65)</b>	(d)
93	Np	237	0.1277287 (39)	0.1226882 (36)	0.1094230 (39)	0.1085265 (28)	(i)
94	Pu	239	0.1245782 (15)	0.11952120 (69)			(h)
94	Pu	244	0.1245705 (25)	0.1195140 (23)	0.1066611 (18)	0.1057595 (18)	(i)
95	Am	243	0.1215158 (24)	0.1164463 (33)	0.1039794 (17)	0.1030803 (17)	(i)
96	Cm	248	0.1185427 (23)	0.1134635 (21)	0.1013753 (17)	0.1004708 (16)	(i)
97	Bk	249	0.1156630 (54)	0.1105745 (49)	0.0988598 (55)	0.0979514 (54)	(i)
98	Cf	250	0.1128799 (82)	0.1077793 (75)			(i)

References: (a) Schweppe *et al.* (1994); (b) Mooney (1996); (c) Schweppe (1995); (d) Deslattes & Kessler (1985); (e) Hölzer *et al.* (1997); (f) Bearden (1967); (g) Borchert, Hansen, Jonson, Ravn & Desclaux (1980); (h) Borchert (1976); (i) Barreau, Börner, Egidy & Hoff (1982).

theoretical framework (see below) has been undertaken and will be made available in the longer publication and on the web site.

The feature of absorption spectra customarily designated as ‘the absorption edge’ has been variously associated with: the first inflection point of the absorption spectrum; the energy needed to produce a single inner vacancy with the photo-electron ‘at rest at infinity’; or the energy needed to remove an electron from an inner shell and place it in the lowest unoccupied energy level. A general discussion of this question has been given by Parratt (1959). If we choose the second alternative, then it is easy to see that, with some care for symmetry restrictions, one can estimate the absorption-edge energy by combining the binding energy for

any accessible outer shell with the energy of an emission line for which the transition terminus lies in the same outer shell. Of course, this procedure does not focus on the details of absorption thresholds, the locations of which are important for a number of structural applications. On the other hand, our choice gives greater regularity with respect to nuclear charge and facilitates use of electron binding energies, since they are referenced to the Fermi energy or the vacuum.

Electron binding energies have been tabulated for the principal electron shells of all the elements considered in the present table (Fuggle, Burr, Watson, Fabian & Lang, 1974; Cardona & Ley, 1978; Nyholm, Berndtsson & Mårtensson,

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Table 4.2.2.2. *Directly measured L-series reference wavelengths in Å*

Numbers in parentheses are standard uncertainties in the least-significant figures.

Z	Symbol	$L\alpha_2$	$L\alpha_1$	$L\beta_1$	References
36	Kr	7.82032(13)	7.82032(13)	7.574441(98)	(a)
40	Zr	6.07710(48)	6.070250(79)	5.836214(76)	(a)
54	Xe	3.025940(22)	3.016582(15)	2.806553(19)	(b)
60	Nd	2.38079(52)	2.370526(16)	2.167008(19)	(a)
62	Sm	2.210430(24)	2.199873(13)	1.998432(30)	(a)
67	Ho	1.856472(15)	1.845092(17)	1.647484(32)	(a)
68	Er	1.795701(45)	1.784481(20)	1.587466(86)	(a)
69	Tm	1.738003(19)	1.7267720(70)	1.5302410(70)	(a)

References: (a) Mooney (1996); (b) Mooney *et al.* (1992).

1980; Nyholm & Mårtensson, 1980; Lebugle, Axelsson, Nyholm & Mårtensson, 1981; Powell, 1995). The number of values available offers the possibility of consistency checking, since the *K* and *L* shells are connected by emission lines to several final hole states, each of which has (possibly) been evaluated by photoelectron spectroscopy. For each of the elements for which well qualified reference spectra are available, we evaluated edge location estimates using several alternative transition cycles and used the distribution of results to provide a measure of the uncertainty. Comparison of edge estimates obtained by this procedure with experimental data provides a quantitative test of the utility of the chosen approach to edge location estimation. In Table 4.2.2.3, the numerical results in the column labelled 'Emission + binding energies' were obtained by combining emission energies and electron binding energies using all possible redundancies. The estimated uncertainties indicated were obtained from the distribution of the redundant routes. As can be seen, the results are in general agreement with the available directly measured values. Accordingly, we have used this protocol to obtain the edge locations listed in the summary tables below.

### 4.2.2.8. Outline of the theoretical procedures

Only recently has it become possible to understand the relativistic many-body problem in atoms with sufficient detail to permit meaningful calculation of transition energies between hole states (Indelicato & Lindroth, 1992; Mooney, Lindroth, Indelicato, Kessler & Deslattes, 1992; Lindroth & Indelicato, 1993, 1994; Indelicato & Lindroth, 1996). To deal with those hole states for atomic numbers ranging from 10 to 100, one needs to consider five kinds of contributions, all of which must be calculated in a relativistic framework, and the relative influence of which can change strongly as a function of the atomic number:

- (i) nuclear size;
- (ii) relativistic effects (corrections to Coulomb energy, magnetic and retardation energy);
- (iii) Coulomb and Breit correlation;

(iv) radiative (QED) corrections (one- and two-electron Lamb shift *etc.*);

(v) Auger shift.

Such an undertaking, although much more advanced than any other done in the past, still suffers from severe limitations that need to be understood fully to make the best use of the table. The main limitation is probably that most lines are emitted by atoms in an elemental solid or a compound, while the calculation at present deals only with atoms isolated in vacuum. (A purely experimental database would have a similar limitation.) The second limitation is that it is not possible at present to include the coupling between the hole and open outer shells. Coupling between a  $j = \frac{1}{2}$ ,  $j = \frac{3}{2}$  or  $j = \frac{5}{2}$  hole and an external  $3d$  or  $4f$  shell can generate hundreds of levels, with splitting that can reach an eV. One then should calculate all radiative and Auger transition probabilities between hundreds of initial and final states. (The Auger final state would have one extra vacancy, leading eventually to thousands of final states.) Such an approach would give not only the mean line energy but also its shape and would thus be very desirable, but is impossible to do with present day theoretical tools and computers. We have thus limited ourselves to an approach in which one computes the weighted average energy for each hole state, and ignores possible distortion of the line profile due to the coupling between inner vacancies and outer shells.

Since we want to have good predictions for both light and heavy atoms, we have to include relativity non-perturbatively. To get a result approaching  $1 \times 10^{-6}$  for uranium  $K\alpha$  by applying perturbation theory to the Schrödinger equation, for example, one would need to go to order 22 in powers of  $Z\alpha = v/c$ . The natural framework in this case is thus to do a calculation exact to all orders in  $Z\alpha$  by using the Dirac equation. We thus have used many-body methods, based on the Dirac equation, in which the main contributions to the transition energy are evaluated using the Dirac-Fock method. We use the Breit operator for the electron-electron interaction, to include magnetic (spin-spin, spin-other orbit and orbit-orbit interactions in the lower orders in  $Z\alpha$  and  $(v/c)^2$  retardation effects. Higher-order retardation effects are also included.