***International Tables for Crystallography* (2006). Vol. C, Section 4.2.1.1, pp. 191–192.**

4.2. X-rays

By U. W. Arndt, D. C. Creagh, R. D. Deslattes, J. H. Hubbell, P. Indelicato, E. G. Kessler Jr and E. Lindroth

4.2.1. Generation of X-rays (By U. W. Arndt)

X-rays are produced by the interaction of charged particles with an electromagnetic field. There are four sources of X-rays that are of interest to the crystallographer.

(1) The bombardment of a target by electrons produces a continuous ('white') X-ray spectrum, called *Bremsstrahlung*, which is accompanied by a number of discrete spectral lines characteristic of the target material. The high-vacuum, or Coolidge, X-ray tube is the most important X-ray source for crystallographic studies.

(2) The decay of natural or artificial radio isotopes is often accompanied by the emission of X-rays. Radioactive X-ray sources are often used for the calibration of X-ray detectors. Mössbauer sources have the narrowest known spectral bandwidth and are used in nuclear resonance scattering studies.

(3) Sources of synchrotron radiation produced by relativistic electrons in orbital motion are of growing importance.

(4) X-rays are also produced in plasmas generated by the bombardment of targets by high-energy laser beams, but to date the yield has been principally in the form of soft X-rays.

The classical text on the generation and properties of X-rays is that by Compton & Allison (1935), which still summarizes much of the information required by crystallographers. There is a more recent comprehensive book by Dyson (1973). X-ray physics has received a new impetus on the one hand through the development of X-ray microprobe analysis dealt with in a number of monographs (Reed, 1975; Scott & Love, 1983) and on the other hand through the increasing utilization of synchrotron-radiation sources (see Subsection 4.2.1.5).

4.2.1.1. *The characteristic line spectrum*

Characteristic X-ray emission originates from the radiative decay of electronically highly excited states of matter. We are concerned mostly with excitation by electron bombardment of a target that results in the emission of spectral lines characteristic of the target elements. The electronic states occurring as initial and final states of a process involving the absorption of emission of X-rays are called *X-ray levels*. Levels involving the removal of one electron from the configuration of the neutral ground state are called *normal X-ray levels* or *diagram levels*.

Table 4.2.1.1 shows the relation between diagram levels and electron configurations. The notation used here is the IUPAC notation (Jenkins, Manne, Robin & Senemaud, 1991), which uses arabic instead of the former roman subscripts for the levels. The IUPAC recommendations are to refer to X-ray lines by writing the initial and final levels separated by a hyphen, *e.g.* Cu K-L_3 and to abandon the Siegbahn (1925) notation, *e.g.* Cu $K\alpha_1$, which is based on the relative intensities of the lines. The correspondence between the two notations is shown in Table 4.2.1.2. Because this substitution has not yet become common practice, however, the Siegbahn notation is retained in Section 4.2.2, in which the wavelengths of the characteristic emission lines and absorption edges are discussed.

Table 4.2.1.1. *Correspondence between X-ray diagram levels and electron configurations; from Jenkins, Manne, Robin & Senemaud (1991), courtesy of IUPAC*

Level	Electron configuration	Level	Electron configuration	Level	Electron configuration
K	$1s^{-1}$	N_1	$4s^{-1}$	O_1	$5s^{-1}$
L_1	$2s^{-1}$	N_2	$4p^{-1}_{1/2}$	O_2	$5p^{-1}_{1/2}$
L_2	$2p^{-1}_{1/2}$	N_3	$4p^{-1}_{3/2}$	O_3	$5p^{-1}_{3/2}$
L_3	$2p^{-1}_{3/2}$	N_4	$4d^{-1}_{3/2}$	O_4	$5d^{-1}_{3/2}$
M_1	$3s^{-1}$	N_5	$4d^{-1}_{5/2}$	O_5	$5d^{-1}_{5/2}$
M_2	$3p^{-1}_{1/2}$	N_6	$4f^{-1}_{5/2}$	O_6	$5f^{-1}_{5/2}$
M_3	$3p^{-1}_{3/2}$	N_7	$4f^{-1}_{7/2}$	O_7	$5f^{-1}_{7/2}$
M_4	$3d^{-1}_{3/2}$				
M_5	$3d^{-1}_{5/2}$				

Table 4.2.1.2. *Correspondence between IUPAC and Siegbahn notations for X-ray diagram lines; from Jenkins, Manne, Robin & Senemaud (1991), courtesy of IUPAC*

Siegbahn	IUPAC	Siegbahn	IUPAC	Siegbahn	IUPAC
$K\alpha_1$	K-L_3	$L\alpha_1$	L_3-M_5	$L\gamma_1$	L_2-N_4
$K\alpha_2$	K-L_2	$L\alpha_2$	L_3-M_4	$L\gamma_2$	L_1-N_2
$K\beta_1$	K-M_3	$L\beta_1$	L_2-M_4	$L\gamma_3$	L_1-N_3
$K\beta^{1}_2$	K-N_3	$L\beta_2$	L_3-N_5	$L\gamma_4$	L_1-O_3
$K\beta^{11}_2$	K-N_2	$L\beta_3$	L_1-M_3	$L\gamma'_4$	L_1-O_2
$K\beta_3$	K-M_2	$L\beta_4$	L_1-M_2	$L\gamma_5$	L_2-N_1
$K\beta^{1}_4$	K-N_5	$L\beta_5$	L_3-$O_{4,5}$	$L\gamma_6$	L_2-O_4
$K\beta^{11}_4$	K-N_4	$L\beta_6$	L_3-N_1	$L\gamma_8$	L_2-O_1
$K\beta_{4x}$	K-N_4	$L\beta_7$	L_3-O_1	$L\gamma'_8$	L_2-$N_{6(7)}$
$K\beta^{1}_5$	K-M_5	$L\beta'_7$	L_3-$N_{6,7}$	L_η	L_2-M_1
$K\beta^{11}_5$	K-M_4	$L\beta_9$	L_1-M_5	Ll	L_3-M_1
		$L\beta_{10}$	L_1-M_4	Ls	L_3-M_3
		$L\beta_{15}$	L_3-N_4	Lt	L_3-M_2
		$L\beta_{17}$	L_2-M_3	Lu	L_3-$N_{6,7}$
				Lv	L_2-$N_{6(7)}$

Siegbahn	IUPAC
$M\alpha_1$	M_5-N_7
$M\alpha_2$	M_5-N_6
$M\beta$	M_4-N_6
$M\gamma$	M_3-N_5
$M\zeta$	$M_{4,5}$-$N_{2,3}$

In the case of unresolved lines, such as K-L_2 and K-L_3, the recommended IUPAC notation is K-$L_{2,3}$.

4.2.1.1.1. *The intensity of characteristic lines*

The efficiency of the production of characteristic radiation has been calculated by a number of authors (see, for example, Dyson, 1973, Chap. 3). For a particular line, it depends on the fluorescence yield, that is the probability that the decay of an excited state leads to the emission of a photon, on the statistical weights of the X-ray levels involved, on the effects of the penetration and slowing down of the bombarding electrons in the target, on the fraction of electrons back-scattered out of the target, and on the contribution caused by fluorescent X-rays produced indirectly by the continuous spectrum. The *emerging* X-ray intensity is further affected by the partial absorption of the generated X-rays in the target.

Dyson (1973) has also reviewed calculations and measurements made of the *relative* intensities of different lines in the K spectrum. The ratio of the $K\alpha_2$ to $K\alpha_3$ intensities is very close to

0.5 for Z between 23 and 48. The ratio of $K\beta_3$ to $K\alpha_2$ rises fairly linearly with Z from 0.2 at $Z = 20$ to 0.4 at $Z = 80$ and that of $K\beta_1$ to $K\alpha_2$ is near zero at $Z = 29$ and rises linearly with Z to about 0.1 at $Z = 80$. Relative intensities of lines in the L spectrum are given by Goldberg (1961).

Green & Cosslett (1968) have made extensive measurements of the efficiency of the production of characteristic radiation for a number of targets and for a range of electron accelerating voltages. Their results can be expressed empirically in the form

$$N_K/4\pi = N_0/4\pi(E_0 - E_K - 1)^{1.63}, \qquad (4.2.1.1)$$

where $N_K/4\pi$ is the *generated* number of $K\alpha$ photons per steradian per incident electron, N_0 is a function of the atomic number of the target, E_0 is the electron energy in keV and E_K is the excitation potential in keV. It should be noted that $N_K/4\pi$ decreases with increasing Z.

For a copper target, this expression becomes

$$N_K/4\pi = 1.8 \times 10^{-6}\,(E_0 - 8.9)^{1.63} \qquad (4.2.1.2)$$

or

$$N'_K/4\pi = 1.1 \times 10^{10}\,(E_0 - 8.9)^{1.63}, \qquad (4.2.1.3)$$

where $N'_K/4\pi$ is the number of $K\alpha$ photons per steradian per second per milliampere of tube current.

These expressions are probably accurate to within a factor of 2 up to values of E_0/E_K of about 10. Guo & Wu (1985) found a linear relationship for the *emerging* number of photons with electron energy in the range $2 < E_0/E_K < 5$.

To obtain the number of photons that *emerge* from the target, the above expressions have to be corrected for absorption of the generated radiation in the target. The number of photons emerging at an angle φ to the surface, for normal electron incidence, is usually written

$$N_\varphi/4\pi = f(\chi)N/4\pi, \qquad (4.2.1.4)$$

where $\chi = (\mu/\rho)\operatorname{cosec}\varphi$ (Castaing & Descamps, 1955). Green (1963) gives experimental values of the correction factor $f(\chi)$ for a series of targets over a range of electron energies. His curves for a copper target are given in Fig. 4.2.1.1. It will be noticed that the correction factor increases with increasing electron energy since the effective depth of X-ray generation increases with voltage. As a result, curves of N_φ as a function of E_0 have a broad maximum that is displaced towards lower voltages as φ decreases, as shown in the experimental curves for copper K radiation due to Metchnik & Tomlin (1963) (Fig. 4.2.1.2). For very small take-off angles, therefore, X-ray tubes should be operated at lower than customary voltages. Note that the values in Fig. 4.2.1.2 agree to within ~40% with those of Green & Cosslett. $f(\chi)$ at constant E_0/E_K increases with increasing Z, thus partly compensating for the decrease in N_K, especially at small values of φ. A recent re-examination of the characteristic X-ray flux from Cr, Cu, Mo, Ag and W targets has been carried out by Honkimaki, Sleight & Suortti (1990).

4.2.1.2. *The continuous spectrum*

The shape of the continuous spectrum from a thick target is very simple: I_ν, the energy per unit frequency band in the spectrum, is given by the expression derived by Kramers (1923):

$$I_\nu = AZ(\nu_0 - \nu) + BZ^2, \qquad (4.2.1.5)$$

where Z is the atomic number of the target and A and B are constants independent of the applied voltage E_0. B/A is of the order of 0.0025 so that the term in Z^2 can usually be neglected (Fig. 4.2.1.3). ν_0 is the maximum frequency in the spectrum, *i.e.* the Duane–Hunt limit at which the entire energy of the bombarding electrons is converted into the quantum energy of the emitted photon, where

$$H\nu_0 = hc/\lambda_0 = E_0. \qquad (4.2.1.6)$$

Using the latest adjusted values of the fundamental constants (Cohen & Taylor, 1987):

$$\begin{aligned} hc &= 1.23984244 \pm 0.00000037 \times 10^{-6}\ \text{eV m} \\ &= 12.3984244 \pm 0.0000037\ \text{keV Å}. \end{aligned}$$

Equation (4.2.1.5) can be rewritten in a number of forms. If $\mathrm{d}N_E$ is the number of photons of energy E per incident electron,

$$\mathrm{d}N_E = bZ(E_0/E - 1)\,\mathrm{d}E, \qquad (4.2.1.7)$$

where $b \sim 2 \times 10^{-9}$ photons eV^{-1} electron^{-1}, and is known as Kramer's constant.

From (4.2.1.7), it follows that the total energy in the continuous spectrum per electron is

$$\int_0^{E_0} E\,\mathrm{d}N_E = bZE_0^2/2. \qquad (4.2.1.8)$$

Since the energy of the bombarding electron is E_0, the efficiency of production of the continuous radiation is

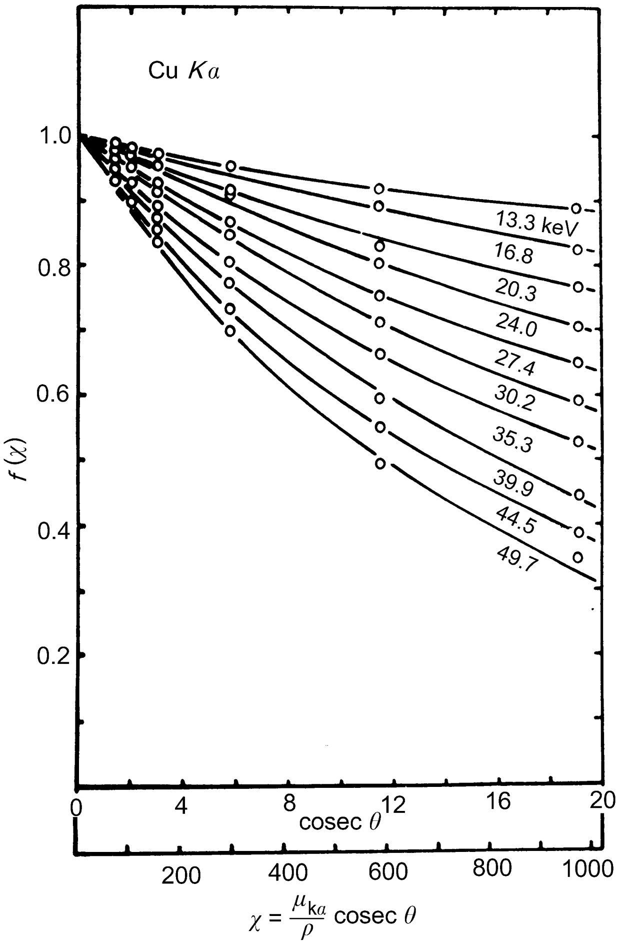

Fig. 4.2.1.1. $f(\chi)$ curves for Cu K-L_3 at a series of different accelerating voltages (in kV). From Green (1963).