which peaks at the alkali configurations and becomes smaller as the screening effect subsides.

9.7 X-RAY SPECTRA AND MOSELEY'S LAW

Electronic transitions within the inner shells of heavier atoms are accompanied by large energy transfers. If the excess energy is carried off by a photon, x rays are emitted at specific wavelengths peculiar to the emitting atom. This explains why discrete x-ray lines are produced when energetic electrons bombard a metal target, as discussed earlier in Section 3.5.

The inner electrons of high Z elements are bound tightly to the atom, because they see a nuclear charge essentially unscreened by the remaining electrons. Consider the case of molybdenum (Mo), with atomic number $Z = 42$ (see Table 9.2). The innermost, or K shell, electrons have $n = 1$ and energy (from Equation 8.38)

$$E_1 = -\frac{ke^2}{2a_0}\left\{\frac{Z^2}{1^2}\right\} = -(13.6\text{ eV})(42)^2 = -23990.4\text{ eV}$$

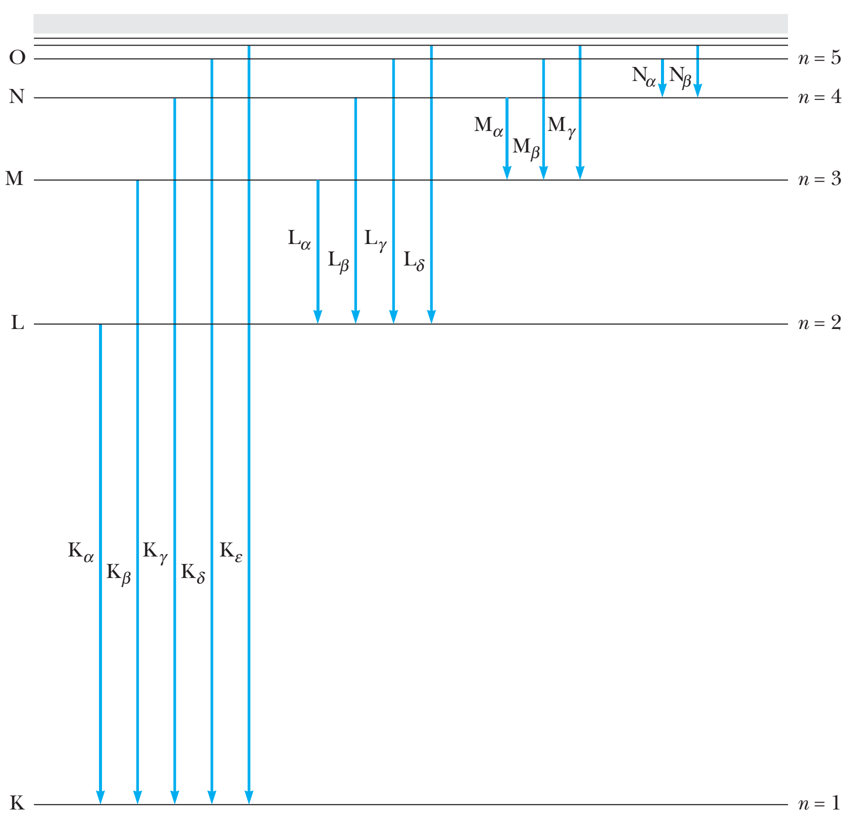

Figure 9.17 Origin of x-ray spectra. The K series (K_α, K_β, K_γ, . . .) originates with electrons in higher-lying shells making a downward transition to fill a vacancy in the K shell. In the same way, the filling of vacancies created in higher shells produces the L series, the M series, and so on.

Thus, approximately 24 keV must be supplied to dislodge a K shell electron from the Mo atom.[8] Energies of this magnitude are routinely delivered via electron impact: electrons accelerated to kilovolt energies collide with atoms of a molybdenum target, giving up most or all of their energy to one atom in a single collision. If large enough, the collision energy may excite one of the K shell electrons to a higher vacant level or free it from the atom altogether. (Recall there are two electrons in a filled K shell.) In either case, a vacancy, or *hole*, is left behind. This hole is quickly filled by another, higher-lying atomic electron, with the energy of transition released in the form of a photon. The exact energy (and wavelength) of the escaping photon depends on the energy of the electron filling the vacancy, giving rise to an entire K series of emission lines denoted in order of increasing energy (decreasing wavelength) by K_α, K_β, K_γ, ... In the same way, the filling of vacancies left in higher shells produces the L series, the M series, and so on, as illustrated in Figure 9.17.

Henry G. J. Moseley (1887–1915) discovered a direct way to measure Z, the atomic number, from the characteristic x-ray wavelength emitted by an element. Moseley's work not only established the correct sequence of elements in the periodic table but also provided another confirmation of the Bohr model of the atom, in this case at x-ray energies. One wonders what other major discoveries Moseley would have made if he had not been killed in action at the age of 27 in Turkey in the first world war. (*University of Oxford, Museum of the History of Science/Courtesy AIP Niels Bohr Library*)

[8] In contrast, only 7.10 eV (the ionization energy from Table 9.2) is required to free the outermost, or 5*s*, electron.

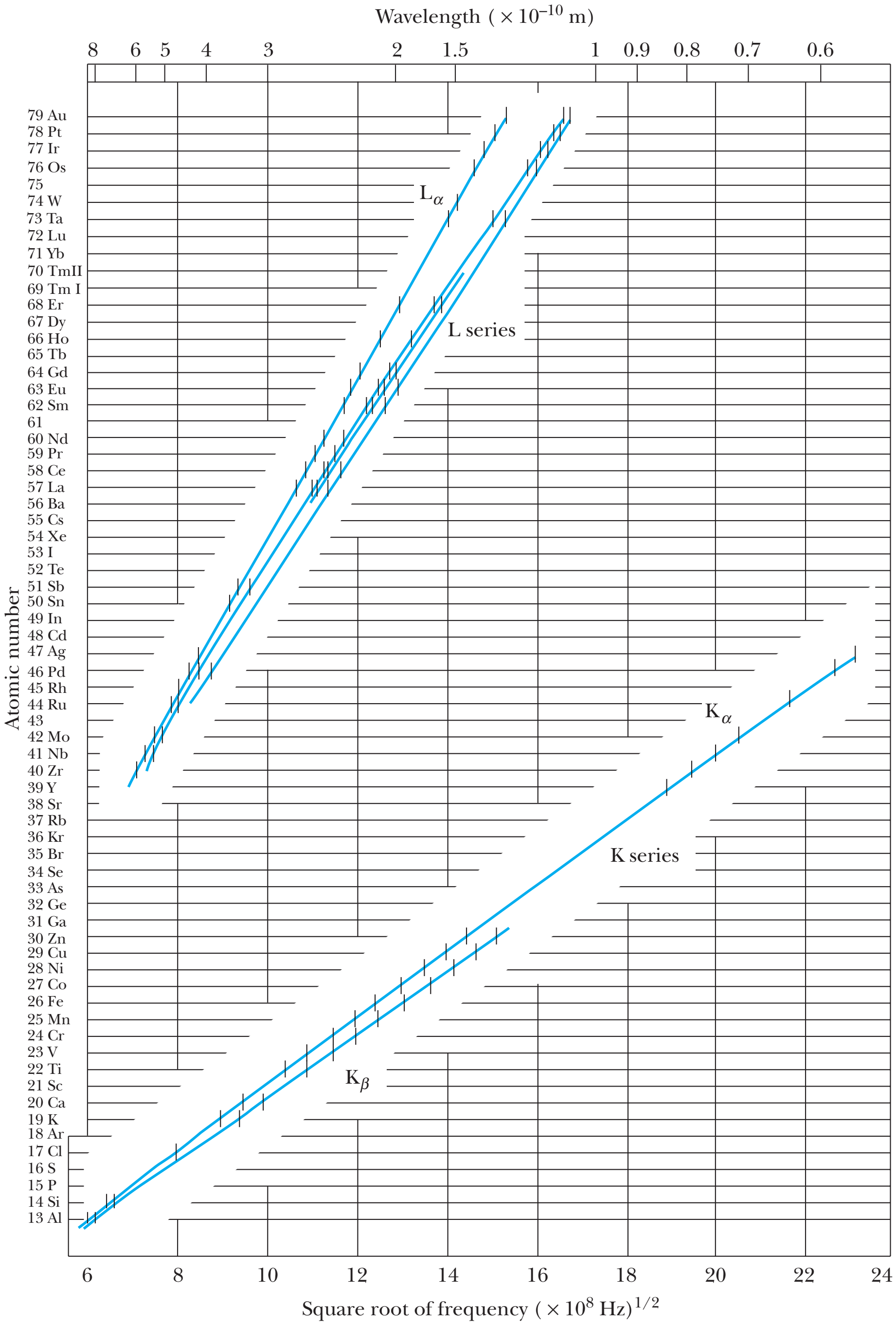

Figure 9.18 The original data of Moseley showing the relationship between atomic number Z and the characteristic x-ray frequencies. The gaps at $Z = 43$, 61, and 75 represent elements unknown at the time of Moseley's work. (There are also several errors in the atomic number designations for the elements.) (© *From H. G. J. Moseley,* Philos. Mag. *(6), 27:703, 1914*)

The energy of the longest-wavelength photons in a series can be estimated from simple screening arguments. For the K_α line, the K shell vacancy is filled by an electron from the L shell $(n = 2)$. But an electron in the L shell is partially screened from the nucleus by the one remaining K shell electron and so sees a nuclear charge of only $Z - 1$. Thus, the energy of the K_α photon can be approximated as an $n = 2$ to $n = 1$ transition in a one-electron atom with an effective nuclear charge of $Z - 1$:

$$E[K_\alpha] = -\frac{ke^2}{2a_0}\frac{(Z-1)^2}{2^2} + \frac{ke^2}{2a_0}\frac{(Z-1)^2}{1^2} = \frac{ke^2}{2a_0}\frac{3(Z-1)^2}{4} \tag{9.26}$$

For molybdenum $(Z = 42)$, this is $E[K_\alpha] = 17.146$ keV, corresponding to a wavelength

$$\lambda[K_\alpha] = \frac{hc}{E[K_\alpha]} = \frac{12.4\ \text{keV}\cdot\text{Å}}{17.146\ \text{keV}} = 0.723\ \text{Å}$$

For comparison, the observed K_α line of molybdenum has wavelength 0.7095 Å, in reasonable agreement with our calculation.

In a series of careful experiments conducted from 1913 to 1914, the British physicist H. G. J. Moseley measured the wavelength of K_α lines for numerous elements and confirmed the validity of Equation 9.26, known as **Moseley's law.** According to Moseley's law, a plot of the square root of photon frequency $(E/h)^{1/2}$ versus atomic number Z should yield a straight line. Such a **Moseley plot,** as it is called, is reproduced here as Figure 9.18. Before Moseley's work, atomic numbers were mere placeholders for the elements appearing in the periodic table, the elements being ordered according to their mass. By measuring their K_α lines, Moseley was able to establish the correct sequence of elements in the periodic table, a sequence properly based on atomic number rather than atomic mass. The gaps in Moseley's data at $Z = 43$, 61, and 75 represent elements unknown at the time of his work.

SUMMARY

The magnetic behavior of atoms is characterized by their **magnetic moment.** The orbital moment of an atomic electron is proportional to its orbital angular momentum:

$$\boldsymbol{\mu} = \frac{-e}{2m_e}\mathbf{L} \tag{9.1}$$

The constant of proportionality, $-e/2m_e$, is called the **gyromagnetic ratio.** Since $\mathbf{L}$ is subject to space quantization, so too is the atomic moment $\boldsymbol{\mu}$. Atomic moments are measured in **Bohr magnetons,** $\mu_B = e\hbar/2m_e$; the SI value of μ_B is 9.27×10^{-24} J/T.

An atom subjected to an external magnetic field $\mathbf{B}$ experiences a magnetic torque, which results in precession of the moment vector $\boldsymbol{\mu}$ about the field vector $\mathbf{B}$. The frequency of precession is the **Larmor frequency** ω_L given by

$$\omega_L = \frac{eB}{2m_e} \tag{9.5}$$