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The tube is not uniformly sensitive across its diameter. The maximum sensitivity is confined to the cylindrical volume shown cross-hatched in the figure. The diameter of this sensitive area depends on the gas filling and the geometry of the tube. For maximum efficiency, the X-ray beam should be directed along and close to the anode, but should not strike it. Geiger counters are not critically temperature-dependent. Linearity of response is limited by the dead-time following the discharge initiated by the absorption of a quantum and the magnification of the few hundred ions produced to some millions by their acceleration under the electric field. To produce this amplification, a certain minimum threshold voltage is required. Above this minimum, there is a plateau extending for several hundred volts within which the number of quanta detected is essentially independent of the applied voltage and the size of the pulses is essentially independent of the energy of the absorbed quantum.

Geiger counters are simple to use and show little deterioration even after prolonged use. However, since the pulses are all of about the same size, pulse-height discrimination cannot be used, and the long dead-time limits linearity of response unless special monitoring circuits are used (Eastabrook & Hughes, 1953). They have been almost completely superseded by other types of counter, described in Sections 7.1.3.–7.1.8.

7.1.3. Proportional counters (By W. Parrish)

7.1.3.1. *The detector system*

The commonest types of detector for both powder and single-crystal diffractometry are proportional counters and especially scintillation counters (Section 7.1.4). The detector system consists of the detector itself, a high-voltage power supply, a single-channel pulse-height analyser, and a scaling circuit, as shown schematically in Fig. 2.3.3.5. For position-sensitive detectors (Section 7.1.3.3) and solid-state detectors (Sections 7.1.4.2 and 7.1.5), multichannel analysers are necessary. The X-ray manufacturers and a number of electronic companies provide complete detector systems, often integrated with the computer data-collection system.

7.1.3.2. *Proportional counters*

Proportional counters are available in various sizes and gas fillings. A typical detector is a metal cylinder about 2 cm in diameter and 8–10 cm long, with central wire anode and 0.13 mm Be side window, Fig. 7.1.2.1(*b*). Some have an opposite exit window to transmit the unabsorbed beam and thus avoid fluorescence from the wall. The tube may be filled with Xe to atmospheric pressure for high absorption, and a small amount of quenching gas such as CO_2 or CH_4 is added to limit the discharge. When an X-ray quantum is absorbed, the discharge current is the sum of the Townsend avalanches of the secondary electrons and the gas amplification is about 10^4. A charge-sensitive preamplifier is generally used. Some proportional counters are filled to several atmospheres pressure to increase the gas absorption. Very thin organic film windows are used for very long wavelengths as in fluorescence spectroscopy. They may transmit moisture, and gas may migrate through them so that flow counters are used to replenish the gas. This requires careful control of the pressure to avoid changes in the counting efficiency.

7.1.3.3. *Position-sensitive detectors*

One variety of position-sensitive detector, in which the photon absorptions in different regions are counted separately, is a special type of proportional counter. The following description applies primarily to one-dimensional detectors for powder diffractometry; two-dimensional (area) detectors are treated in Section 7.1.6.

Position-sensitive detectors (PSD's) are being used in increasing number for various powder-diffraction studies. They have the great advantage of simultaneously recording a much larger region of the pattern than conventional counters. The difference in receiving apertures determines the gain in time. The position at which each quantum is detected is determined electronically by the system computer and stored in a multichannel analyser. There is a digital addition of each incident photon address and the angular address of the diffractometer.

The PSD's are available in short straight form and as longer detectors with curvature to match the diffractometer focusing circle. The short detectors can be used in a stationary position to cover a small angular range or scanned. Göbel (1982) developed a high-speed method using a short (8° window) scanning PSD with 50 µm linear resolution in the diffractometer geometry shown in Fig. 2.3.1.12(*b*). He was able to record at speeds of a hundred or more degrees a minute, and patterns with reasonably good statistical precision in several tens of degrees a minute. This is faster than conventional energy-dispersive diffraction and has the advantage of much higher resolution.

The PSD should be selected to match best the diffraction geometry. The detector is sensitive across the 1–2 cm gas-absorption path. If the diffracted rays are not perpendicular to the window, the parallax causes broadening and loss of resolution. This becomes important in the focusing geometries and can be minimized if the diffractometer and specimen focusing circles are nearly coincident. A large loss of resolution would occur in the conventional geometry, Fig. 2.3.1.3, because only the central ray of a single reflection would be normal to the window. The problem is minimized in powder-camera geometry with a thin rod specimen, Fig. 2.3.4.1(*a*), where the entire pattern can be recorded with a long, curved PSD (Ballon, Comparat & Pouxe, 1983); see also Shishiguchi, Minato & Hashizume (1986), Lehmann, Christensen, Fjellvåg, Feidenhans'l & Nielsen (1987), Wölfel (1983), and Foster & Wölfel (1988).

7.1.3.4. *Resolution, discrimination, efficiency*

The topics of energy resolution, pulse-height discrimination, quantum-counting efficiency, and linearity are common to proportional, scintillation and solid-state counters, and are treated in Subsections 7.1.4.3.–7.1.4.5.

7.1.4. Scintillation and solid-state detectors (By W. Parrish)

7.1.4.1. *Scintillation counters*

The most frequently used detector is the scintillation counter (Parrish & Kohler, 1956). It has two elements: a fluorescent crystal and a photomultiplier tube, Fig. 7.1.2.1(*c*). For X-ray diffraction, a cleaved single-crystal plate of optically clear NaI activated with about 1% Tl in solid solution is used. The crystal is hygroscopic and is hermetically sealed in a holder with thin Be entrance window and glass back to transmit the visible-light scintillations. The size and shape of the crystal can be selected, but is usually a 2 cm diameter disc or a rectangle $20 \times 4 \times 1$ mm thick. A small thin crystal has been used to reduce the background from radioactive samples (Kohler & Parrish, 1955). A viscous mounting fluid with about the same refractive index as the glass is used to reduce light reflection and to attach it to the end of the photomultiplier tube. The crystal and photomultiplier are mounted in a light-tight cylinder surrounded by an antimagnetic foil. The high X-ray absorption of the crystal provides a high quantum-counting efficiency.

A Cu $K\alpha$ quantum produces about 500 visible photons of average wavelength 4100 Å in the scintillation crystal (which matches the maximum spectral sensitivity of the photomultiplier), but only about 25 will be effective in the photomultiplier operation. High-speed versions with special pulse-height analysers have recently become available; they are linear to about 1% at 10^5 counts s^{-1} and can be used at rates approaching 10^6 counts s^{-1} (see Rigaku Corporation, 1990).

The detector system is as described in Subsection 7.1.3.1.

7.1.4.2. *Solid-state detectors*

The following description applies primarily to the use of solid-state detectors in powder diffractometry. Further details of their operation and their use in energy-dispersive diffractometry are treated in Section 7.1.5.

The most common form of solid-state detector consists of a lithium-drifted silicon crystal Si(Li) and liquid-nitrogen Dewar. A perfect single crystal is used with very thin gold film on the front surface for electrical contact. The first amplifier stage is a field-effect transistor (FET). The unit must be kept at liquid-nitrogen temperature at all times (even when not in use) to prevent Li diffusion and to reduce the dark current when in use. The unit is large and heavy and, if not used in a stationary position, a robust detector arm is required, which is usually counter-balanced. The crystal is made with different-size sensitive areas and the resolution is somewhat dependent on the size of the area. In the detector process, the number of free charge carriers (the electron and electron–hole pairs) generated during the X-ray absorption changes the conductivity of the crystal and is proportional to the energy of the X-ray quantum. Details of the mechanism are given in several books [see, for example, Heinrich, Newbury, Myklebust & Fiori (1981) and Russ (1984)].

Intrinsic germanium detectors have higher absorption than silicon detectors, but they have lower energy resolution and there are more interferences from escape peaks. A mercuric iodide (HgI_2) detector can be operated at room temperature and has high absorption (Nissenbaum, Levi, Burger, Schieber & Burshtein, 1984). They have poorer resolution than Si or Ge detectors but can be improved to FWHM = 200 eV at 5.9 keV by cooling to 269 K (Ames, Drummond, Iwanczyk & Dabrowski, 1983).

A small (about 16.5×10 cm), lightweight (3.2 kg) silicon detector with Peltier thermoelectric cooling is available (*e.g.* Kevex Corporation, 1990). This development has supplanted a number of the methods of collecting powder data. The elimination of the liquid-nitrogen Dewar and the compact size makes it possible to replace conventional detectors and the diffracted-beam monochromator in scanning powder diffractometry. The spectrum is displayed on a small screen and the window of the analyser can be set closely on the energy distribution obtained from a powder reflection to transmit, say, only Cu $K\alpha$. The monochromator can be eliminated for a large gain of intensity without loss of pattern resolution. The energy resolution is FWHM $\approx$ 195 eV at 5.9 keV. Elemental analysis can be performed by energy-dispersive fluorescence, and the background can be restricted to the narrow energy window selected. Bish & Chipera (1989) used it to obtain a 3–4 times increase of intensity, the same pattern resolution, and lower tails than with a graphite monochromator and scintillation counter in conventional diffractometry. The major limitation at present is the limited input intensity that can be handled. The limiting (total) count rate is about 10^4 counts s^{-1} and the detector becomes markedly nonlinear at 2×10^4 counts s^{-1}. Internal dead-time corrections can extend the range by increasing the counting times.

7.1.4.3. *Energy resolution and pulse-amplitude discrimination*

The pulse amplitudes are proportional to the energy e of the absorbed X-ray quantum so that electronic methods can be used to reduce the background from other wavelengths and sources. The rejection range is limited by the energy resolution of the detector. As noted above, the pulse amplitudes have distributions that vary around the average value A, Figs. 7.1.4.1(*a*),(*b*). The FWHM of the distribution increases linearly with increasing e (eV) and is proportional to $e^{1/2}$, *i.e.* it improves inversely with $\lambda^{1/2}$. The ratio FWHM/A (expressed in %) is a measure of the energy resolution at a given wavelength; the smaller the ratio the better the resolution. For example, as e increases from 5 to 45 keV, the FWHM approximately doubles while FWHM/e decreases from 5 to 1%. The resolution of proportional counters is about 18% for Cu $K\alpha$ and somewhat better for high-pressure gas fillings; in scintillation counters, it is about 45%. The solid-state detectors have much better resolution. The best are about 2.4% (145 eV) at 5.9 keV (which is the energy of Mn K X-rays from a radioactive ^{55}Fe source used as a standard for calibration).

The electronics include a high-voltage power supply to about 1200 V for scintillation counters and 2000–3000 V for proportional counters, and a single-channel pulse-amplitude discriminator. The latter contains pulse-shaping circuits and the amplifier, and is designed to transmit pulses whose amplitudes lie within the selected range. The lower level rejects all pulses below the selected level and the upper level rejects the higher amplitudes (Figs. 7.1.4.1*a*, *b*). The range selected is called the window and determines the pulse amplitudes that will be counted by the scaling circuit.

The multichannel analyser is generally used with solid-state detectors. It may have up to 8000 channels and sorts the pulses from the amplifier into individual channels according to their amplitudes, which are proportional to the X-ray photon energies. The pattern can be stored and displayed on a CRT screen, but nowadays a personal computer with a suitable interface card is normally used in place of the analyser. Various programs are available for peak-energy identification, spectral stripping, intensity determination, and similar data-reduction requirements. The limiting count rate that can be handled by the electronics is determined by the total number of photons striking the detector. Pulse-pileup rejectors are used to stop counting momentarily when another pulse is too close in time to allow the original pulse to return to the baseline voltage. A live-time correction extends the counting period beyond the clock time to compensate for the time the analyser is gated off. About 50 000 counts s^{-1} is the maximum rate so that the individual powder reflections have a much smaller number of pulses. If good statistical accuracy is required, the count times are, therefore, much longer than in conventional diffractometry.

For a given e, the pulse amplitudes of scintillation and proportional counters increase with increasing voltage (internal gain) and amplifier setting (external gain). The detector must be operated in the plateau region for the wavelength used (Fig. 7.1.4.1*c*). The counts are measured as a function of the voltage and/or gain, and the plateau begins where there is no further significant increase of intensity. In selecting the operating conditions, one should avoid excessively high voltages and amplifier gains, which may cause noise pulses and unstable operation. Optimum settings can be determined by experiment and from manufacturer's instructions. The average pulse height should be set at about 20–25% of the full range of the pulse-height analyser. Lower settings move the low-energy tail into the noise, and high settings broaden the distribution and may be too wide for the window.

The pulse-amplitude distribution can be measured with a narrow (1–3 V) upper level and increasing the lower level by small equal steps. When making this calibration, it is advisable to keep the incident count rate below 10^4 counts s^{-1} to avoid nonlinearity and pulse pileup. A plot of intensity *versus* lower-level setting shows the distribution, Fig. 7.1.4.1(*a*). In some electronics, this can be done automatically and displayed on a screen. The window should be set symmetrically around the peak with the window decreasing the characteristic line intensity only a few per cent below that obtained with the lower-level set to remove only the circuit noise. The intensity change can be seen with a rate meter. Narrow windows cause a larger percentage loss of intensity than the decrease in background and, hence, the peak-to-background ratio is reduced. Asymmetric windows are sometimes used to decrease the fluorescence background.

7.1.4.4. *Quantum-counting efficiency and linearity*

The quantum-counting efficiency E of the detector, its variation with wavelength, and electronic discrimination determine the response to the X-ray spectrum. E is determined by

$$E = f_T f_A, \tag{7.1.4.1}$$

where f_T is the fraction of the incident radiation transmitted by the window (usually 0.013 mm Be) and f_A is the fraction absorbed in the detector (scintillation crystal or proportional-counter gas). E varies with wavelength as shown in Fig. 7.1.4.1(*d*). The scintillation counter has a nearly uniform E approaching 100% across the spectrum and detects the short-wavelength continuous radiation with about the same efficiency as the spectral lines. The gas-filled counters have a lower E for the short wavelengths and, therefore, may have a slightly lower inherent background; high-pressure gas counters have a higher and more uniform spectral efficiency.

The effectiveness of electronic discrimination with a scintillation counter is shown in Fig. 2.3.5.3(*c*) for 50 kV Cu target radiation. The method cannot separate the $K\alpha$-doublet components because of their small energy difference, and has little effect on the $K\beta$ peak. The results are greatly enhanced by the addition of a $K\beta$ filter, which removes most of the $K\beta$ peak and a portion of the continuous radiation below the filter absorption

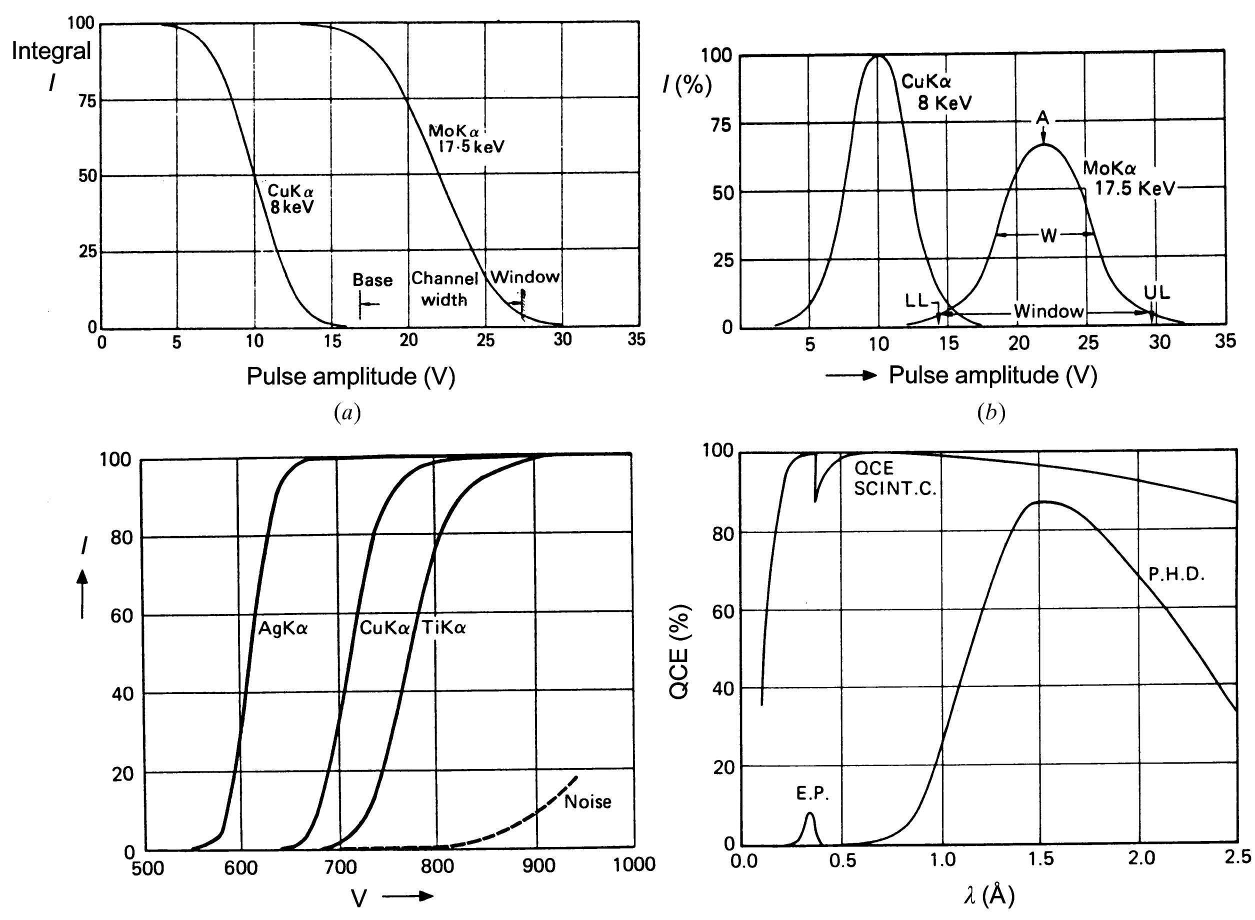

Fig. 7.1.4.1. Calculated pulse-amplitude distributions of Cu $K\alpha$ and Mo $K\alpha$ in the form of (*a*) integral curves and (*b*) differential curves. Resolution W/A for Cu $K\alpha = 50\%$. Analyser settings show window between lower level (*LL*) and upper level (*UL*). (*c*) Plateaux of scintillation counter for various wavelengths and fixed amplifier gain. Curves normalized to same intensity at highest voltage. Noise curve is plotted in counts s^{-1}. Curves can be moved to higher or lower voltages by changing amplifier gain. (*d*) Calculated quantum-counting efficiency (QCE) of scintillation counter as a function of wavelength (top curve) and its reduction when the pulse-height analyser is set for 90% Cu $K\alpha$. E.P. is escape peak at lower left.

edge, Fig. 2.3.5.3(*b*). The combination of discrimination and filter produces mainly the $K\alpha$ doublet, Fig. 2.3.5.3(*d*). Spectral analysis of the background of a non-fluorescence powder sample using this method with 50 kV Cu radiation and a scintillation counter shows it to be 50–90% characteristic radiation.

The linearity of the system is determined by the dead-time of the detector, and the resolving times of the pulse-height analyser and scaling circuit. The observed intensity $n_{\rm obs}$ is related to the effective dead-time of the system $\tau_{\rm eff}$ by the relation

$$n_{\rm true} = n_{\rm obs}/(1 - \tau_{\rm eff}\, n_{\rm obs}). \qquad (7.1.4.2)$$

The value of $\tau_{\rm eff}$ can be measured with an oscilloscope, or with the multiple-foil method in which a number of equal absorption foils (*e.g.* Al 0.025 mm or Ni 0.018 mm for Cu $K\alpha$) are inserted in the beam one or two at a time. To make certain monochromatic radiation is used, a single-crystal plate such as Si(111), which has no significant second order, and low X-ray tube voltage are employed. The linearity is determined from a regression calculation. A less accurate method is to plot $n_{\rm obs}$ on a log scale against the number of foils on a linear scale. Recent developments in high-speed scintillation counters have extended the linearity to the 10^5–10^6 counts s^{-1} range.

7.1.4.5. *Escape peaks*

The pulse-amplitude distribution may have two or more peaks, even when monochromatic X-rays are used (Parrish, 1966). Absorption of the incident X-rays by the counter-tube gas or scintillation crystal may cause X-ray fluorescence. If this is reabsorbed in the active volume of the counter only one pulse is produced of average amplitude A_1 proportional to the incident X-ray quantum energy e_1 (k = constant)

$$A_1 = ke_1. \qquad (7.1.4.3)$$

However, the gas or crystal has a low absorption coefficient for its own fluorescent radiation, hence, some quanta of the latter of energy e_2 may escape from the active volume of the counter, the amount depending on the geometry of the tube, gas, windows, *etc*. The average amplitude A_2 of the escape pulses is

$$A_2 = k(e_1 - e_2). \qquad (7.1.4.4)$$

Thus,

$$A_1 - A_2 = ke_2. \qquad (7.1.4.5)$$

The pulse-height analyser discriminates against pulses only on the basis of their amplitudes. When it is set to detect X-rays of energy e_0, it is also sensitive to X-rays of energy $e_0 + e_2$. For example, when using an NaI scintillation counter for Cu $K\alpha$, $e_0 = 8$ keV, and for the escape X-rays I $K\alpha$, $e_2 = 28.5$ keV. A pulse-height analyser set to detect X-rays of energy 8 keV is also sensitive to X-rays of energy 36.5 keV, because, from equations (7.1.4.3) and (7.1.4.4),

$$A_0 = k.8 = k(36.5 - 28.5) = A_2. \qquad (7.1.4.6)$$

In Figs. 2.3.5.3(*c*), (*d*) and 7.1.4.1(*d*), the escape peak E.P. shows clearly at 0.35 Å, the wavelength of 36.5 keV X-rays. There may be a number of weak escape peaks arising from the stronger powder reflections. In practice, the escape peak should not be confused with a small-angle reflection. It can be tested by reducing the X-ray tube voltage to below the absorption-edge energy of the element in the detector from which it arises.

7.1.5. Energy-dispersive detectors (By B. Buras and L. Gerward)

In white-beam energy-dispersive X-ray diffraction, the spectral distribution of the diffracted beam is measured either with a semiconductor detector (low-momentum resolution) or with a scanning-crystal monochromator (high-momentum resolution) (see Subsection 2.5.1.3). Commercially available detectors are made of lithium-drifted silicon or germanium [denoted Si(Li) and Ge(Li), respectively], or high-purity germanium (HPGe). There are, however, other materials that are good candidates for making energy-dispersive detectors.

The semiconductor detector can be regarded as the solid-state analogue of the ionization chamber. Charge carriers of opposite sign (electrons and holes) are produced by the X-ray photons. They drift in the applied electric field of the electrodes and are converted to a voltage pulse by a charge-sensitive preamplifier. The energy required for creating an electron–hole pair is 3.9 eV in silicon and 3.0 eV in germanium. The number of electron–hole pairs is proportional to the energy of the absorbed photon (the intrinsic efficiency is discussed below). There is no intrinsic gain and one has to rely on external amplification. The preamplifier employs an input field-effect transistor (FET), cooled in an integral assembly with the detector crystal in order to reduce thermal noise. Usually the detector is operated at liquid-nitrogen temperature. However, Peltier-cooled silicon detectors are available, removing the maintenance concerns of cryostat cooling. The basic counting system consists further of an amplifier, producing a near-Gaussian pulse shape, and a multichannel pulse-height analyser. It is common to use an

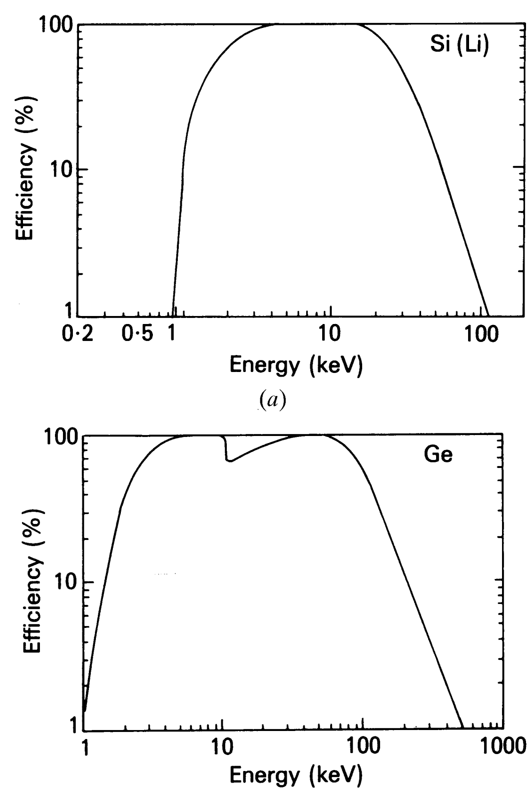

Fig. 7.1.5.1. Intrinsic efficiency of semiconductor detectors. The dimensions are selected to give typical best values of the energy resolution. (*a*) Si(Li), detector thickness 3 mm, Be-window thickness 25 µm. (*b*) HPGe, detector thickness 5 mm, Be-window thickness 50 µm.