altered. The energy and momentum can be considered as decoupled; the recoil momentum is transferred to the crystal as a whole and, if this is fixed in the laboratory, to the earth. The velocity of recoil, and hence the kinetic energy, is effectively zero. The vibrational energy of the lattice is quantized; if the lowest allowable quantum of vibrational energy (the lowest phonon energy) is large compared to the recoil energy, there will be a finite probability of recoilless decay. Since this energy peak is not Döppler broadened, it is nearly monochromatic, and the lower limit to the width is set by the lifetime of the excited state and the uncertainty principle. In actual cases there is usually additional broadening due to imperfect motion and other instrumental problems, relaxation phenomena, and other factors.

A wide variety of nuclei display Mössbauer resonance, but by far the most useful from the standpoint of the study of solids is ^{57}Fe. The process by which the 14·4 keV Mössbauer gamma ray is produced is outlined in Fig. 1(a), and in this paper we shall limit ourselves to studies involving this isotope.

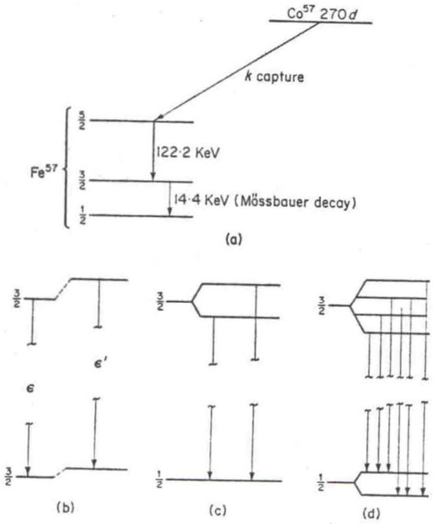

FIG. 1. Basic concepts for ^{57}Co–^{57}Fe Mössbauer system. (a) ^{57}Co decay, (b) isomer shift, (c) electric field, (d) magnetic field.

The Mössbauer effect is capable of giving information concerning a number of different aspects of the nuclear environment. First and most basic is the isomer shift. The process of decay by gamma emission involves a transition of the nucleus from an excited state to its ground state. The difference in energy between these states is slightly but measurably perturbed by the electronic environment of the nucleus. Specifically, it is affected by those electronic wave functions having non-zero amplitude at the nucleus; and these must be states of zero angular momentum (s states). The electronic configuration of atomic iron is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. The $1s$ and $2s$ wave functions surely have significant amplitude at the nucleus, but they are largely isolated from the surrounding atoms and can tell us little about changes in the environment. The $4s$ electrons interact strongly with the neighbouring atoms, and while they are largely shielded from the nucleus, they contribute significantly to studies of isomer shift changes, particularly in metals. In ionic states of iron the $4s$ levels are usually assumed to be sparsely occupied. The $3s$ electrons do not interact to any extent with the surrounding atoms or ions, although they have their radial maximum at very nearly the same point as the $3d$ electrons which do interact with the neighbouring atoms. Changes in the $3d$ states with changing environment will then affect the degree of shielding of the $3s$ electrons from the nucleus, which will be reflected in changes in the observed difference in nuclear energy levels, that is in the isomer shift (see Fig. 1(b)). Thus, a dilute solution of ^{57}Co (^{57}Fe) in copper will not be in resonance with ^{57}Fe dissolved in chromium, or with ^{57}Fe in FeCl$_2$. If one now imparts a motion to the source with respect to the absorber, when the Döppler velocity just compensates for the difference in the isomer shifts of the two materials, resonance is obtained. A Mössbauer spectrometer is a device for measuring the velocities necessary to obtain resonance, and the differences in value of the isomer shift, $\Delta\epsilon$, in different environments is expressed in terms of the relative velocity necessary to obtain resonance. Spectrometers are widely described in the literature (Frauenfelder, 1963; Wertheim, 1964: also for high pressure, Pipkorn *et al.*, 1964; DeBrunner *et al.*, 1966), and will not be discussed here. For ^{57}Fe the energy differences (that is isomer shift differences) from material to material are of the order of a mm/sec or a fraction thereof. It is perfectly practical to measure differences smaller than 0·1 mm/sec, which corresponds to a thermal energy difference of 10^{-5}°C, or $\sim 10^{-5}$ calories ($\sim 10^{-9}$ eV) which illustrates the sensitivity of the technique.

The isomer shift is described by the equation:

$$\Delta\epsilon = \alpha[\psi_S^2(0) - \psi_A^2(0)] \qquad (1)$$