

The alloys now had to be prepared as Mössbauer sources, of dimensions compatible with the high-pressure techniques to be used. First they were pressed and cold rolled to 0.001-in. thickness. Such thin samples are advantageous both for minimizing self-absorption of Mössbauer γ rays and for obtaining uniform reproducible pressures. A rectangular section 0.120 $\times$ 0.014 in. was then fashioned, with a tab being left on one end. This rectangular section was suspended by its tab in a 1:1 $\text{NH}_4\text{OH-H}_2\text{O}$ electroplating solution which contained radioactive Co^{57} as a complex. (The Co^{57} was obtained from the Oak Ridge National Laboratory, Oak Ridge, Tenn. and from the New England Nuclear Corp., Boston, Mass.) A cathodic lead was attached to the tab, and with a platinum anode an applied voltage of 2 V produced a plating current of about 15 μA . The electroplating was continued until 1.5 mCi of Co^{57} had been deposited on the sample surface, usually a period of several days. The tab was then cut off.

The heat treatment necessary for diffusing the Co^{57} into the body of the sample, and for the final anneal, was found to require great care, as it was important to avoid contaminating the sample. Due to the small sample size (0.120 $\times$ 0.014 $\times$ 0.001 in.) a small amount of contamination from the sample holder could, and at first did, produce in the Mössbauer spectra very noticeable irreproducible effects, which were quite dependent on the amount of diffusion time. The following technique finally yielded reproducible consistent results: Several containers were fashioned from two 0.75-in. segments of 0.375- and 0.312-in.-diam molybdenum rod. Each segment was drilled out through most of its length, such that the i.d. of the large-diameter segment was a bit greater than the o.d. of the small-diameter one. Thus the larger piece formed a loosely fitting highly overlapping cover for the smaller piece. The containers were then chemically polished and heated in vacuum to 1000 $^\circ\text{C}$ for 1 h for degassing. Next some aluminum oxide wool was cleaned in hot aqua regia, filtered, stuffed into the Mo containers, and heated in vacuum at 1000 $^\circ\text{C}$ for $\frac{1}{2}$ h. The wool which emerged was clean, fluffy, and pure white. The radioactive samples were then set on wool in the centers of separate Mo containers, held in place by more wool, and enclosed with the Mo covers. The containers were put in a quartz tube which was sealed into a diffusion-pump vacuum system and surrounded by a cylindrical resistance furnace. The samples were thus "open" to the vacuum, yet shielded from the quartz by the closed Mo containers and prevented from contacting the Mo by the aluminum oxide wool. The heat treatment was carried out under a vacuum of 2×10^{-7} Torr. The heating was performed slowly so that the vacuum

was always better than 2×10^{-6} Torr. The diffusion was accomplished at 800 $^\circ\text{C}$ for 12 h, the temperature was brought up to 950 $^\circ\text{C}$ for 1 h for annealing, and a slow cooling process was then begun. The cooling period was divided approximately into three equal time intervals, the first ending just above the Curie temperature, the second just below the Curie temperature, and the third at room temperature. Since the highest Curie temperature encountered was ~ 150 $^\circ\text{C}$, most of the time was spent at low temperatures. The intent was to attempt to form large domains, and thus reduce to a minimum possible complications resulting from domain-wall effects. With the above careful technique, cooling periods of 10 and 25 days yielded identical Mössbauer results. The radioactive foil was now cut into three pieces, to be used in three separate pressure runs. Each piece was 0.040 $\times$ 0.014 $\times$ 0.001 in. and contained ~ 0.5 mCi of radioactivity.

The possibility of having altered the alloy compositions through introduction of the radioactive Co must be considered, especially since some non-radioactive Co^{59} was included along with the Co^{57} . A 1.5-mCi sample of Co^{57} radioactivity ($t_{1/2} = 270$ days) requires that 2×10^{15} Co^{57} nuclei be present. According to the manufacturer, there may have been several times this amount of Co^{59} also present, as well as some Fe^{57} depending on the age of the material. From the known lattice constant of the alloy (or from the density) it can be shown that a sample of the size used here contains $\sim 2 \times 10^{18}$ atoms. Thus about 0.2- to 0.3-at.% Co was added to each sample. Hence we take the Co content of the Mössbauer sources to be (5.2, 8.2, 9.2, 12.2, and 15.2) ± 0.3 -at.% Co. The Fe^{57} contained in the initial radioactive solution was not plated onto the sample, since Fe does not complex with the electroplating solution. Thus the Fe^{57} content of each sample depends on the amount of time elapsed since the plating. After one year, a sample would be ~ 0.06 -at.% Fe^{57} .

The PdCo alloys thus prepared are random substitutional alloys⁴⁶ in polycrystalline form. Our observations therefore sense an average over all directions of hyperfine field. Due both to the rolling process in the formation of the foil and to the demagnetizing energy of the foil, however, it is unlikely that the orientations of the crystallites are truly random.⁴⁷ Such directional phenomena do not affect the quantities of interest here, which are the magnitudes of the fields $|H_i|$.

The single-line absorber used in this work was a 0.00025-in. thick No. 303 stainless-steel foil enriched with 1.5 mg/cm² of Fe^{57} . The enriching was done by electroplating a layer of Ni, then Fe^{57} , onto the foil surface and heating for 24 h under vacuum at 700 $^\circ\text{C}$. The process was then repeated

until the desired Fe^{57} area density had been achieved. The Ni helped the Fe^{57} adhere to the foil surface, and was also necessary to keep the alloy in a nonmagnetic phase. The Fe^{57} was obtained from Oak Ridge.

B. High-Pressure Techniques

The high-pressure techniques employed here have been described in detail elsewhere.^{43,48,49} An essential modification was made, however, in the accommodation of the foil samples. The high-pressure cell is pictured in Fig. 1. It was found that pressure runs were markedly improved (with regard to the magnitude of the pressures obtained and their reproducibility) when the button backing the foil was made of the same 85-wt% boron-15-wt% lithium-hydride mix as the outer pellet, instead of pyrophyllite as was used previously.⁴⁹ The cell shown in Fig. 1 is placed between the flats of Bridgman anvils and compressed uniaxially in a hydraulic press. (See Fig. 2 of Ref. 48.) Friction prevents the B-LiH from squirting out between the anvil flats and the B-LiH transmits the applied force quasi-hydrostatically to the sample.⁵⁰

It should be appreciated that the foil sample sits *on edge* relative to the direction of applied force by the press. The γ rays emitted from the foil source have only to pass through a small thickness of low-absorbing B-LiH in order to reach the Mössbauer spectrometer. The limiting pressures for this work (~ 200 kbar) are set not by the maximum attainable sample pressures, but by plastic flow of the anvil faces which eventually bows them and cuts off the Mössbauer radiation.

The pressure calibration of the present high-pressure cell was originally determined with x rays, using the high-pressure x-ray techniques of Perez-Albuerné *et al.*⁵⁰ Periodic checks of the quality of the critical cell-loading technique were performed by loading a bismuth foil, measuring

resistance vs applied pressure, and noting discontinuities at the 25- and 75-kbar transition points.

C. Mössbauer Techniques

The Mössbauer spectrometer employed in this work has been described in Ref. 48, and in more detail in Ref. 43. The moving-absorber configuration was used here, the source being the pressurized sample under study. The computer program for fitting the raw Mössbauer data was essentially that of Chrisman and Tumolillo.⁵¹ The fitted quantities of most interest here are the line positions, since the magnitude of the six-line splitting is proportional to the Fe^{57} hyperfine field $|H_i|$, and the centroid of the six-line spectrum gives the isomer shift. (There were no electric-quadrupole effects observed in this work.) The spectra of each pressure run were calibrated against a standard to determine the hyperfine-field scale (the number of kOe corresponding to an observed line splitting) and the isomer-shift energy scale (the number of mm/sec of Doppler shift corresponding to the width of each channel of the multichannel analyzer memory). The standard was a source of Fe^{57} in ferromagnetic iron metal, at atmospheric pressure. For each pressure run this iron spectrum was taken with the same absorber and the same absorber motion as used in the run itself. The ratio of the line splittings for the spectrum of a given sample to the splittings for iron (in channel numbers) is then the ratio of $|H_i|_{\text{sample}}$ to $|H_i|_{\text{iron}}$, and the latter was taken to be 330 kOe.^{52,53} The data of Preston *et al.*⁵² on the relative positions of the iron lines in mm/sec (at 294 °K) were used to determine the isomer-shift energy calibration, i.e., the number of mm/sec per channel.

III. DATA AND INTERPRETATION

A. Data

Some typical Mössbauer spectra are shown in Figs. 2(a), 2(b), and 2(c). All data were taken at constant temperature $T = 297$ °K. The solid curves are computer fits (superpositions of Lorentzians) to the experimental data points. The effect of pressure on the hyperfine field for $\text{Pd}_{0.91}\text{Co}_{0.09}$ is seen to be quite dramatic. We wish to stress the fact that *all pressure effects observed here are reversible*, i.e., upon release of pressure the hyperfine fields return very close to their initial $p = 0$ values, the $x = 0.08$ and $x = 0.09$ spectra collapsing back to single lines. Figure 3 shows the pressure and volume dependences of the Fe^{57} hyperfine fields, at 297 °K, observed for the four alloys in this experiment. [No hyperfine field was observed for $\text{Pd}_{0.95}\text{Co}_{0.05}$, since it remained paramagnetic at all pressures (cf. Table I).] The solid lines in Fig. 3 are simply smoothed curves drawn

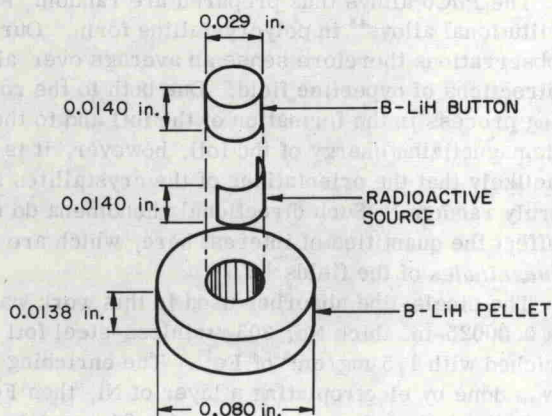


FIG. 1. High-pressure cell.