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## Mössbauer Study of $\text{Co}^{57}(\text{Fe}^{57})$ in Cobaltous Oxide at High Pressure\*

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We report a room-temperature study of the Mössbauer effect of divalent  $\text{Co}^{57}(\text{Fe}^{57})$  in cobaltous oxide up to pressures of about 250 kbar. As pressure is applied, the velocity spectrum unfolds from a single line into a hyperfine pattern in a manner consistent with the measured increase of the Néel temperature with pressure as reported by D. Bloch. The pressure dependences of the internal magnetic field, electric field gradient, and isomer shift are described.

### INTRODUCTION

COBALTOUS oxide has the NaCl structure above its Néel temperature,  $T_N = 291^\circ\text{K}$ . Below this temperature it becomes tetragonal. Previous Mössbauer studies at atmospheric pressure of  $\text{Co}^{57}(\text{Fe}^{57})$  in this compound at several temperatures are consistent with this assignment.<sup>1-3</sup> Pressure studies of CoO in the range 0-6 kbar show  $\partial T_N / \partial P = 0.60^\circ\text{K}/\text{kbar}$ .<sup>4</sup> One thus expects a room-temperature Mössbauer study of this compound at pressures from 0-250 kbar to show a marked magnetic behavior.

### EXPERIMENT

The radioactive CoO samples were made by adding 0.6 mg of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  as carrier to the desired activity (up to 4 mCi) of  $\text{Co}^{57}$  in HCl solution. The activity was then transferred, drop by drop, to a platinum boat (formed by pressing a 0.005-in foil of platinum into a die with a blunt pencil). The resulting mixture of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was dried at  $110^\circ\text{C}$ . It was then converted to  $\text{Co}_3\text{O}_4$  by heating it slowly in air to  $750^\circ\text{C}$  and then decomposed to CoO in vacuum at above  $1000^\circ\text{C}$  for one hour. Fresh, nonradioactive material prepared in this manner was observed by x-ray analysis to be essentially pure CoO.

Previous high-pressure Mössbauer experiments have employed samples which were in the form of a foil.<sup>5,6</sup> Since the present sample was in the form of a powder, loading of the high-pressure cell was accomplished by

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<sup>1</sup> G. K. Wertheim, Phys. Rev. **124**, 764 (1961).

<sup>2</sup> A. J. Bearden, P. L. Mattern, and T. R. Hart, Rev. Mod. Phys. **36**, 470 (1964).

<sup>3</sup> The first two references have also opened up the question as to the possibility of observing trivalent  $\text{Fe}^{57}$ , in this compound, which forms as an aftereffect of the nuclear decay of divalent  $\text{Co}^{57}$ .

<sup>4</sup> D. Bloch, Ann. Phys. (Paris) (to be published).

<sup>5</sup> D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De Pasquali, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. **135**, A1604 (1964).

<sup>6</sup> C. K. Edge, R. Ingalls, P. Debrunner, H. G. Drickamer, and H. Frauenfelder, Phys. Rev. **138**, A729 (1965).

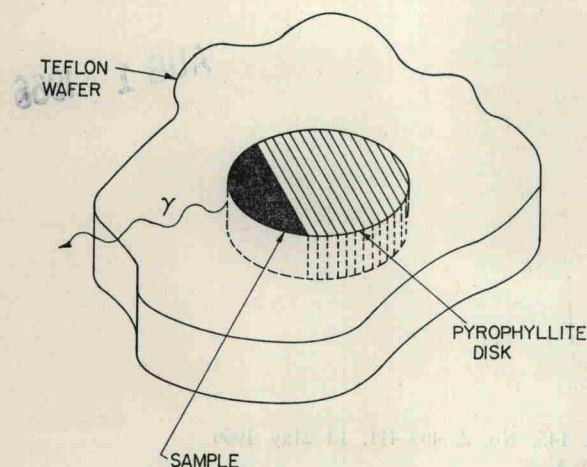


Fig. 1. Detail of the Teflon mold used in forming the source disk.

modifying the central pyrophyllite disk in the general loading scheme first used by Pipkorn *et al.*<sup>5</sup> After carefully clamping a small disk (0.035 in.  $\times$  0.015 in.) of pyrophyllite, a segment of 0.010 in. was sanded off from one edge. The disk was then inserted into a hole 0.035 in. in diam in a Teflon wafer 0.015 in. thick (Fig. 1). The radioactive cobaltous oxide powder was then mixed with as small an amount of epoxy as was required to achieve good binding. This mixture was then inserted into the open segment between the sanded pyrophyllite disk and the Teflon form. The entire assembly was then clamped between two pieces of Teflon and placed in a drying oven at 80°C to cure the epoxy. The resulting disk, containing the source, was then loaded into a pressure cell similar to that described by Pipkorn *et al.*<sup>5</sup> The velocity spectrometer and enriched stainless steel absorber are also described in that work. (With them one obtains an isomer shift of  $-0.09$  mm/sec and line-width of  $\sim 0.6$  mm/sec for a dilute source of  $\text{Co}^{57}$  in metallic iron at atmospheric pressure.)

## RESULTS AND DISCUSSION

The main features of the velocity spectra are qualitatively similar to those found in the temperature study of this system as reported by Wertheim,<sup>1</sup> except, as discussed in the following paragraphs, the fraction of trivalent  $\text{Fe}^{57}$  observed is substantially reduced. At room temperature and atmospheric pressure, the velocity spectrum consists of a narrow emission line consistent with that expected for divalent  $\text{Fe}^{57}$  in a cubic, nonmagnetic environment. As pressure is applied, the pattern broadens and, at sufficiently high pressures, resolves itself into a well-defined hyperfine spectrum (Fig. 2). A computer fit to the data enables a determination of the internal magnetic field  $H_i$  at the  $\text{Fe}^{57}$  nucleus, the results of which are displayed in Fig. 3. For comparison, we also show the temperature de-

pendence of this field down to its saturation value.<sup>1,2,7</sup> It is to be noted that  $H_i$  increases rapidly with increasing pressure, and at 250 kbar reaches a value of  $214 \pm 4$  kOe, which is greater than the saturation value found at low temperatures and atmospheric pressure.<sup>7</sup> This behavior is interpreted as an increase in the superexchange interaction, and with it, the Néel temperature. It is presumably caused by an increase in overlap between the magnetic ions and their oxygen ligands with decreasing volume. Comparison of the  $H_i$  versus  $T$  curve with the  $H_i$  versus  $P$  curve shows that at low pressures, the latter is consistent with the results of Bloch,<sup>4</sup> namely,  $\partial T_N / \partial P \cong 0.6^\circ \text{K/kbar}$ .

In determining  $H_i$  from the velocity spectra, it was found necessary to correct for a small quadrupole interaction (described below) and for a small fraction of stable trivalent  $\text{Fe}^{57}$  impurity. It is immediately obvious from the velocity spectrum taken at 250 kbar that the intensities vary from those found in the normal magnetic spectrum of  $\text{Fe}^{57}$ . We believe that the major cause for this behavior is that a certain fraction of  $\text{Co}_3\text{O}_4$ , remains in the sample after preparation or else

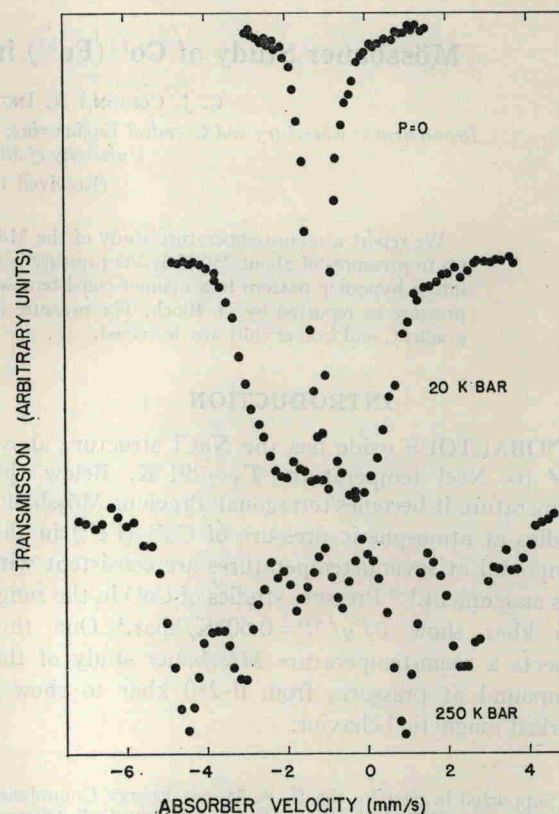


Fig. 2. Room-temperature velocity spectra of  $\text{Co}^{57}$  ( $\text{Fe}^{57}$ ) in  $\text{CoO}$  at several pressures. Positive velocity corresponds to the enriched stainless steel absorber approaching the source.

<sup>7</sup> Along with Wertheim (Ref. 1) it is our observation that  $H_i$  decreases again at temperatures below about 170°K. Contrary to his experiences, however, the saturation value of  $H_i$  which we find at this temperature and atmospheric pressure is about 180 kOe rather than 200 kOe.