

AUG 1 1966

Reprinted from THE PHYSICAL REVIEW, Vol. 145, No. 2, 409-411, 13 May 1966
Printed in U. S. A.

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

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(Received 13 December 1965)

We report a room-temperature study of the Mössbauer effect of divalent Co^{57} (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 Co^{57} (Fe^{57}) in this compound at several temperatures are consistent with this assignment.¹⁻³ Pressure studies of CoO in the range 0-6 kbar show $\partial T_N / \partial P = 0.60^\circ\text{K}/\text{kbar}$.⁴ 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 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°C . It was then converted to Co_3O_4 by heating it slowly in air to 750°C and then decomposed to CoO in vacuum at above 1000°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.^{5,6} Since the present sample was in the form of a powder, loading of the high-pressure cell was accomplished by

* Supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1198 and in part by the U. S. Office of Naval Research under Contract 1834(05).

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¹ G. K. Wertheim, Phys. Rev. **124**, 764 (1961).

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

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

⁴ D. Bloch, Ann. Phys. (Paris) (to be published).

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

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

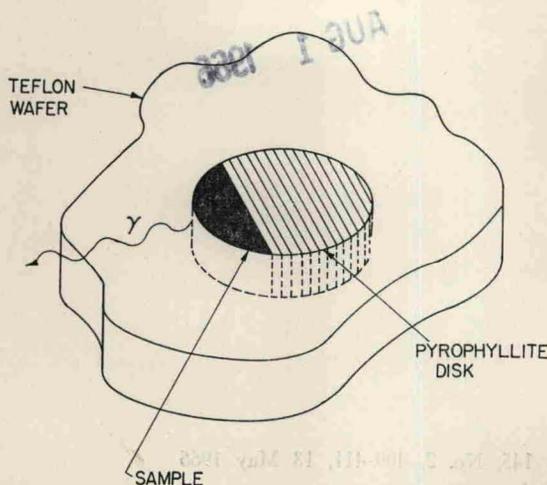


FIG. 1. Detail of the Teflon mold used in forming the source disk.

modifying the central pyrophyllite disk in the general loading scheme first used by Pipkorn *et al.*⁵ 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.*⁵ 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 ~ 0.6 mm/sec for a dilute source of 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,¹ except, as discussed in the following paragraphs, the fraction of trivalent 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 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 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.^{1,2,7} It is to be noted that H_i increases rapidly with increasing pressure, and at 250 kbar reaches a value of 214 ± 4 kOe, which is greater than the saturation value found at low temperatures and atmospheric pressure.⁷ 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,⁴ namely, $\partial T_N / \partial P \approx 0.6^\circ\text{K}/\text{kbar}$.

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 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 Fe^{57} . We believe that the major cause for this behavior is that a certain fraction of Co_3O_4 , remains in the sample after preparation or else

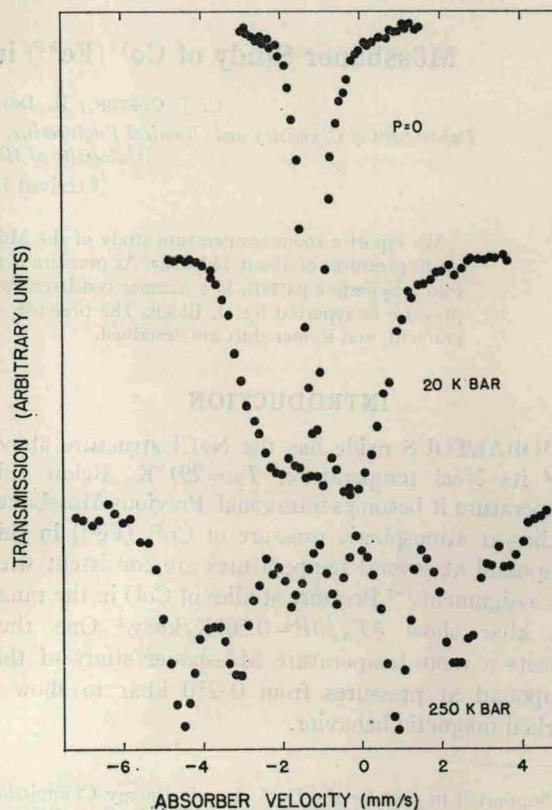


FIG. 2. Room-temperature velocity spectra of Co^{57} (Fe^{57}) in CoO at several pressures. Positive velocity corresponds to the enriched stainless steel absorber approaching the source.

⁷ 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.

actually comes, with time, from CoO which is somewhat unstable at room temperature. One trivalent Fe^{57} absorption line is distinctly visible at approximately $+3.7$ mm/sec. Interpretation of this line as the fifth component in a spectrum associated with a field of 440 kOe and isomer shift of -0.5 mm/sec would place its other members almost directly beneath the first, third, and fifth components of the divalent Fe^{57} pattern, thus causing them to appear too intense. Careful study of the spectrum obtained at atmospheric pressure also reveals that it contains a trivalent Fe^{57} component containing approximately 20% of the total area, a value consistent with the computer decomposition of the data taken at high pressures. From analyses of the Mössbauer spectra of many samples, we have found that even our "best" ones invariably contain between 10 and 20% trivalent Fe^{57} component. Samples prepared differently (i.e., different heat treatment or starting compound), but not studied under pressure, were observed to contain sometimes 40 or 50%.

For the above reasons, we believe that very little (i.e., less than 10%) stable trivalent Fe^{57} is produced by "after effects" of the nuclear decay^{1,8}; that is, of the many trivalent and higher Fe^{57} charge states formed as a result of the electron capture by divalent Co^{57} in CoO , and the subsequent Auger cascade, very nearly all return to the initial divalent state in a time short compared with the 10^{-7} sec half-life of Fe^{57} . This behavior is in contrast with that found in studies involving Co^{57} in several other cobalt compounds.⁸

At high pressures the electric quadrupole coupling is evident from the fact that the relative spacing of divalent Fe^{57} resonance lines is slightly different from what one expects from a pure magnetic interaction. Assuming, therefore, that the electric field gradient tensor (EFG) is small and axially symmetric, it is possible to extract from the data the factor⁹:

$$\epsilon = \frac{1}{8} e^2 q Q (3 \cos^2 \theta - 1),$$

where q is the axial component of the EFG, Q is the quadrupole moment of Fe^{57m} , and θ is the angle between the internal magnetic field and the symmetry axis of the EFG. The computer results consistently showed this quantity to be negative and roughly doubling with pressure from approximately -0.03 mm/sec at 100 kbar to -0.06 mm/sec at 250 kbar. These figures may contain considerable error because, although the crystal structure at high pressures may be tetragonal, just as it is at lower temperatures, we have no direct evidence that the EFG at the Fe^{57} nucleus is axially symmetric, nor do we know the relative orienta-

⁸ R. Ingalls and G. De Pasquali, *Phys. Letters* **15**, 262 (1965).

⁹ G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press Inc., New York, 1964), p. 82.

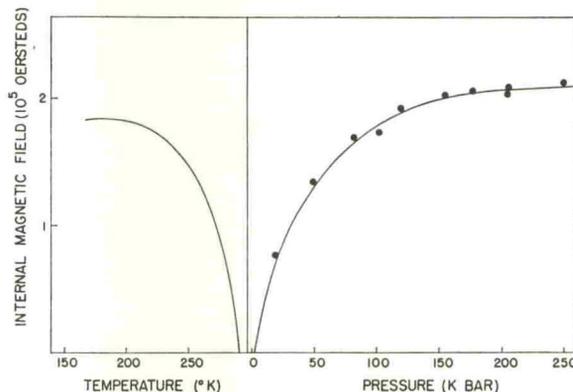


Fig. 3. Graph of the internal magnetic field H_i versus temperature at atmospheric pressure, and also versus pressure at room temperature.

tion of the internal magnetic field with respect to the axes of the EFG. The appreciable trivalent Fe^{57} component of course also reduces their accuracy.

In our study we note that there appears to be a small but consistent decrease in isomer shift of the divalent Fe^{57} pattern from about -1.16 to -1.08 mm/sec over the pressure range covered. These values may, however, also be affected by the above sources of error. This change in isomer shift corresponds to increasing s -electron density at the nucleus with decreasing volume, a behavior that has been found in other experiments.^{5,6,10,11} Here the initial isomer shift is smaller than that generally found in divalent ionic compounds and indicates greater covalent character. As pressure is applied, increasing overlap between the divalent Fe ion and its oxygen ligands could result in a spreading out of the 3d electron distribution accompanied by a subsequent increase in 3s charge density at the nucleus caused by diminished shielding by 3s electrons. A similar behavior presumably occurs with the 3s spin density at the nucleus. The latter would account for the increased saturation value of H_i at high pressures.

ACKNOWLEDGMENTS

We are pleased to thank H. Frauenfelder, P. Debrunner, and G. De Pasquali for their gracious assistance in various phases of this work.

Note added in proof. Our speculation concerning the origin of the trivalent Fe^{57} component has recently been confirmed by James G. Mullen and H. N. Ok [private communication and *Bull. Am. Phys. Soc.* **11**, 267 (1966)].

¹⁰ R. V. Pound, G. B. Benedek, and R. Drever, *Phys. Rev. Letters* **7**, 405 (1961).

¹¹ C. J. Coston, R. Ingalls, and H. G. Drickamer, studies of Co^{57} in CoSO_4 (unpublished).