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 factor[9]:

$$\epsilon = \tfrac{1}{8}e^2qQ(3\cos^2\theta - 1),$$

where $q$ is the axial component of the EFG, $Q$ is the quadrupole moment of $Fe^{57m}$, and $\theta$ 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-
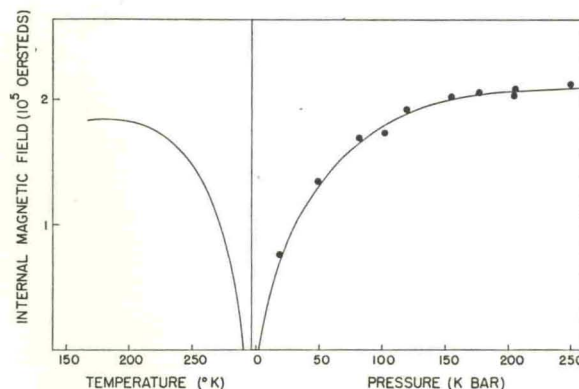


FIG. 3. Graph of the internal magnetic field $H_i$ versus temperature at atmospheric pressure, and also versus pressure at room temperature.

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

*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)].

[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.

[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).