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 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 orientation 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.

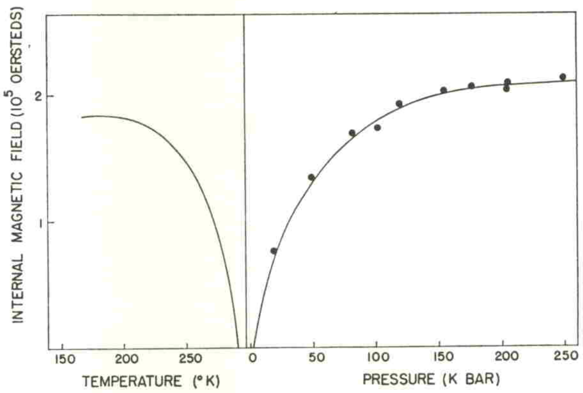

FIG. 3. Graph of the internal magnetic field H_i versus temperature at atmospheric pressure, and also versus pressure at room temperature.

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)].

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