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THE EFFECT OF PRESSURE ON THE MÖSSBAUER EFFECT OF Fe^{57} IN NICKEL METAL

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ABSTRACT

In order to better understand the interaction of the ferromagnetic host with an impurity atom in a dilute alloy, the Mössbauer spectrum of Fe^{57} in nickel metal was studied to a pressure of 80 kbars. A peak in the internal field at the Fe^{57} nucleus was observed at 10 kbars, followed by a slow decrease up to 80 kbars. The initial increase of the internal field with pressure is given by

$$\frac{d\ln H}{dP} = 10.2 \times 10^{-4}\ \mathrm{kbar}^{-1}.$$

The isomer shift over the entire pressure range is given by

$$\frac{d(IS)}{dP} = -4.15 \times 10^{-5}\ \mathrm{cm/sec/kbar}.$$

These results are discussed as they relate to other pressure studies on the properties of pure nickel and iron.

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I. INTRODUCTION

Mössbauer studies of Fe^{57} in iron have illustrated the usefulness of the Mössbauer effect in solid state physics. By studying the volume dependence of the internal field and isomer shift of Fe^{57} in different environments, we may further understand the origin and relationship of these nuclear parameters to the bulk properties of solids. In this work, the pressure dependence of the Fe^{57} Mössbauer effect in nickel metal has been carefully studied to a maximum pressure of 80 kbars.

Nickel metal has the face-centered-cubic structure at 1 atmosphere and room temperature.[1] It is ferromagnetic up to the Curie temperature, 360°C.[1] Patrick[2] observed an 0.35°C/kbar increase of the Curie temperature, T_c, of nickel up to a pressure of 8 kbars. More recently, Bloch and Pauthenet[3] observed an increase in T_c of 0.32°C/kbar up to 4 kbars. Other high pressure investigations have revealed discontinuities in the slopes of the pressure coefficient of resistivity $(1/P)(\Delta R/Ro)$ versus pressure[4] and in the volume versus pressure curves.[5] These results are reproduced in Fig. 1. A discontinuous change in the slope of the pressure-volume curve or the resistivity-pressure curve is usually characteristic of a second order phase transition, such as the Curie or Néel temperature in magnetic materials. Resistivity kinks were used to study the pressure dependence of the Néel points of dysprosium[6] and chromium.[7] In contrast, Lawson[4] has pointed out that resistivity kinks and compressibility anomalies may be related to complicated changes in the band structure and not necessarily to second order phase transitions. The origin of these anomalies in the behavior of nickel metal is unknown.

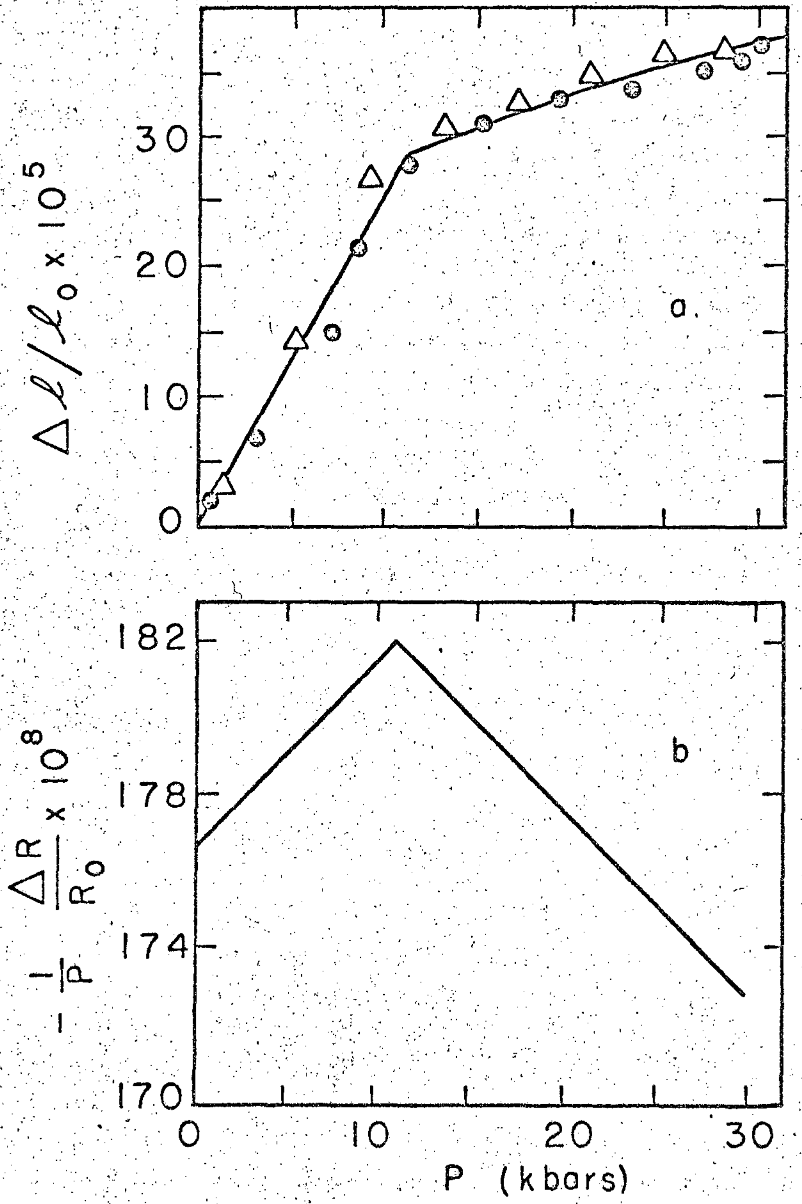

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Fig. 1. a) Differential change of length of nickel with pressure (after Bridgman[5]). b) Pressure coefficient of resistance of nickel as a function of pressure (after Lawson[4]).

Drickamer et al. have studied the Mössbauer effect of Fe^{57} in nickel up to a pressure of 250 kbars.[8] This work was primarily concerned with the very high pressure region above 60 kbars. The internal field and isomer shift vary slowly with pressure. These results are compared with those of the present investigation in Section III. NMR studies of Ni^{61} in nickel show a large increase in the internal field with pressure up to 7 kbars.[9] The relative increase in hyperfine field, H, is given by

$$\frac{d\ln H}{dP} = +\,8.81 \times 10^{-4}\ \mathrm{kbar}^{-1}. \tag{1}$$

Recently, Dash et al. investigated the Fe^{57} Mössbauer effect in nickel from 77°K to the Curie point.[10] The temperature dependence of the internal field deviated significantly from the temperature dependence of the saturation magnetization. These results were analyzed in terms of localized impurity moments.

The magnitude of the internal magnetic field at 0°K in pure nickel metal is -75 kgauss,[11] compared with a value of -339 kgauss for iron.[12] The value of H at an Fe^{57} nucleus in nickel is -280 kgauss.[10] Table I summarizes the data on internal fields for the pure metals and dilute alloys of iron, cobalt and nickel. It is noted that the field at the iron nucleus in a given metal is in every case larger than the field at the host lattice nucleus. This suggests that the field at an iron nucleus is due largely to its own electrons and depends only slightly on the host magnetization. This effect arises because of the large core contribution to the internal field via core polarization by unpaired 3d electrons localized on the iron impurity nuclei.[18] The variation of the internal field at Fe^{57} nuclei in iron, cobalt, and nickel arises primarily from conduction electron contributions. Since the application of pressure is expected to reflect variations in the electronic distri-

Table I. Magnetic fields in units of 10^5 gauss at transition metal nuclei located in transition metals.

Nuclei at which field is measured	Lattice Atoms		
	Fe	Co	Ni
Fe	3.39[a]	3.29[b]	2.80[c]
Co	2.86[d]	2.15[e]	1.11[f]
Ni	2.52[g]	2.03[g]	0.75[h]

a. Ref. 12
b. Ref. 13
c. Ref. 10
d. Ref. 14
e. Ref. 15
f. Ref. 16
g. Ref. 17
h. Ref. 11

bution of conduction electrons, the pressure dependence of the internal field should be dependent primarily on the host lattice. Table II summarizes data on the pressure dependence of internal fields for various transition metal systems. Indeed, there is a distinct grouping of coefficients according to host. For a more complete discussion of internal fields and review of the present experimental data, see the recent review article by Shirley and Westenbarger.[22]

The present high pressure Mössbauer investigation of Fe^{57} in nickel metal is intended to supplement the earlier high pressure work and further confirm the importance of the host lattice in determining the volume dependence of the internal magnetic field and isomer shift.

Table II. The pressure dependence of the internal field H in transition metal systems

Nucleus	Host	$(d\ln H/dP)\times 10^7 \text{bar}^{-1}$
Ni^{61}	Ni	+8.81[a]
Co^{59}	Ni	+13.8 [a]
Fe^{57}	Ni	+10.2 [b]
Co^{59}	Co	+6.1 [c]
Fe^{57}	Co	+6 [d]
Cu^{63}	Fe	-3.0 [e]
Co^{59}	Fe	+1.6 [e]
Fe^{57}	Fe	-1.69[f]

a. Ref. 9
b. This work
c. Ref. 19
d. Preliminary results of author
e. Ref. 20
f. Ref. 21

II. EXPERIMENTAL

The basic high pressure velocity sweep Mössbauer spectrometer has been described earlier.[23,24] The drive system has been modified to provide either a linear velocity wave form to the moving absorber as described by Zane,[25] or the standard sine wave velocity modulation.

The sources were prepared from nickel rods of quoted purity 99.999%. The samples were rings, 0.184 in. outside diameter, 0.163 in. inside diameter, and 0.007 in. high. These were prepared by electroplating Co^{57} onto a 1/3 segment of the ring and subsequently annealed at 1000°C for five hours. Runs 1 and 2 utilized 8 and 2 millicurie sources, respectively.

The absorber used throughout was an 0.7 mil stainless steel foil made from iron enriched to 91.2% Fe^{57}. This absorber provided a broad unsplit absorption line. A 1 atmosphere spectrum of Fe^{57} in nickel is illustrated in Fig. 2. The spectrum has been smoothed by averaging the raw data over nine adjacent channels to reduce the effect of statistical fluctuations for illustration purposes. Internal field and isomer shift data were calculated by resolving the overlapping lines by least squares analysis on a digital computer. The velocity scale was calibrated by determining the Fe^{57} Mössbauer effect in pure iron which has been accurately determined in previous experiments.[26]

III. RESULTS

The results of this work and previous data[8] on the pressure dependence of the isomer shift and internal field of Fe^{57} in nickel are compiled in Figs. 3 and 4, respectively. In both cases, the data are in agreement within the experimental errors. There appears to be a definite peak in the internal field at approximately 10 kbars. The initial rate of increase in the internal field was calculated by fitting the data from 1 atmosphere to 12.5 kbars to a straight line by least squares analysis. The pressure coefficient of the field is given by

$$\frac{d\ln H}{dP} = + 10.2 \times 10^{-4}\ \text{kbar}^{-1}. \qquad (2)$$

The value of the internal field at atmospheric pressure is 270 ± 5 kgauss. Similarly, a least squares fit of the isomer shift data yields

$$\frac{d(IS)}{dP} = - 4.15 \times 10^{-5}\ \text{cm/sec/kbar}, \qquad (3)$$

or in terms of the relative volume change by

$$\frac{d(IS)}{d(V/Vo)} = 0.0789\ \text{cm/sec}. \qquad (4)$$

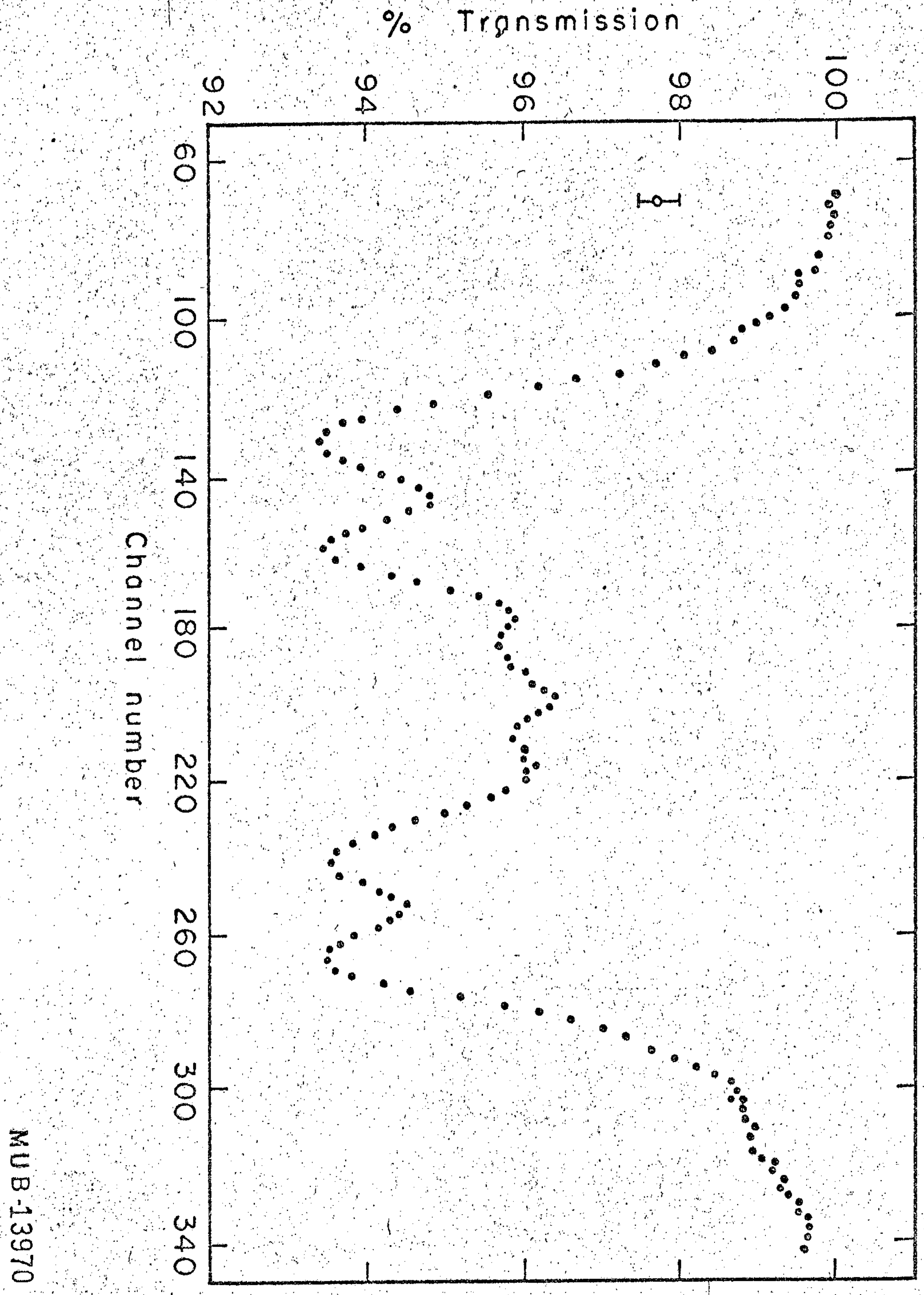

Fig. 2 Mössbauer spectrum of Fe^{57} in nickel at 1 atmosphere.

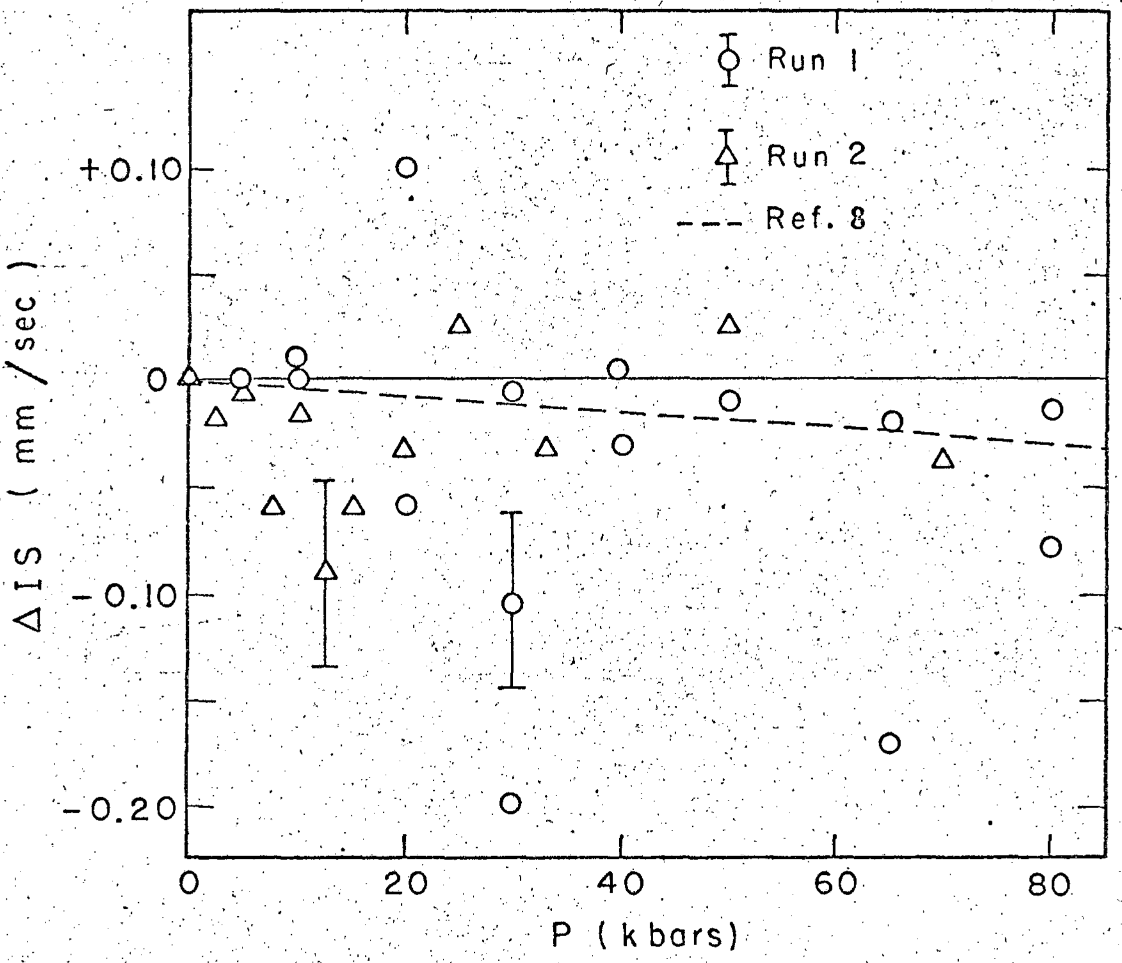

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Fig. 3 Variation of the isomer shift of Fe^{57} in nickel as a function of pressure. Error flags are indicated on single points.

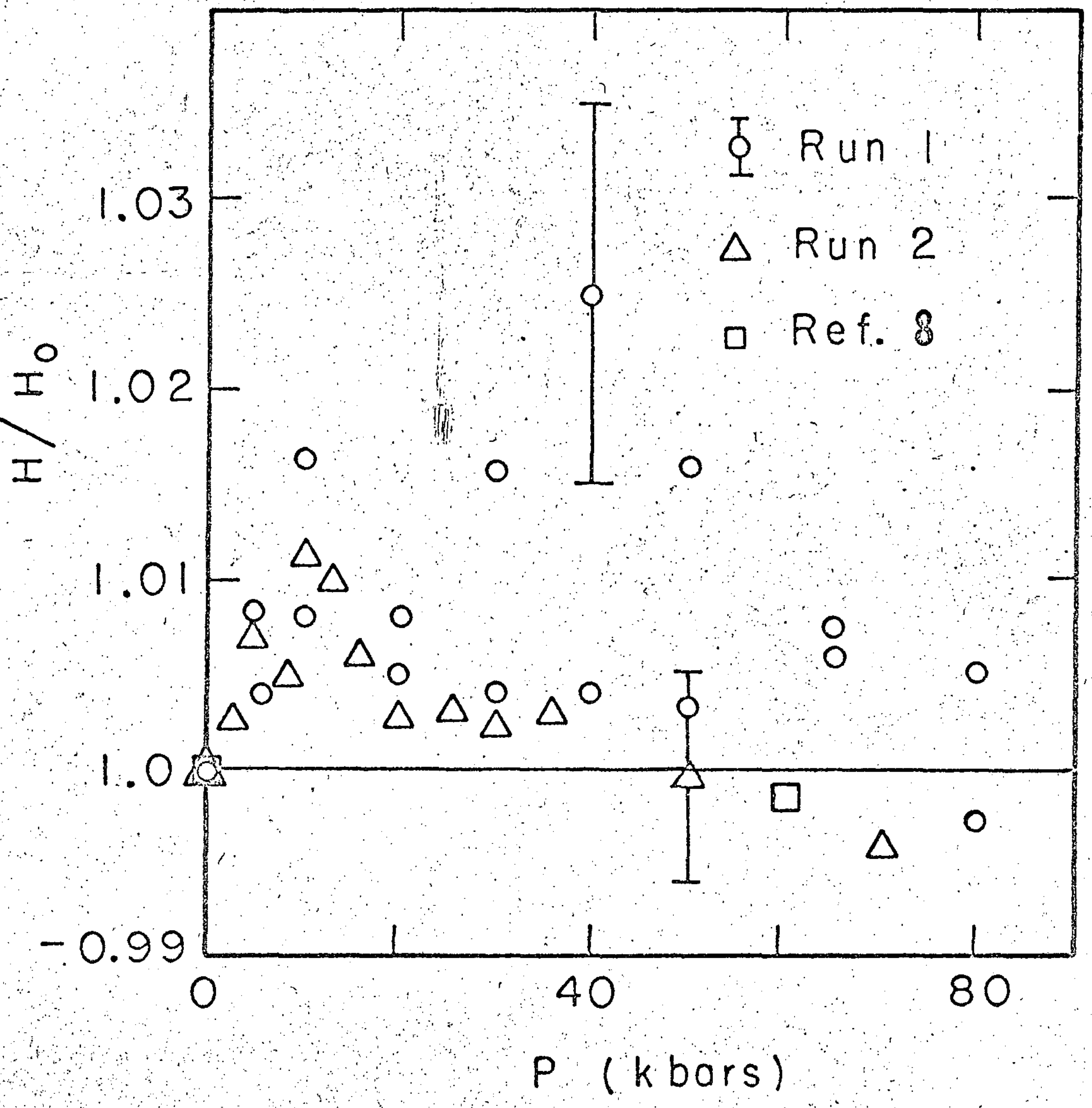

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Fig. 4 Variation of the internal magnetic field of Fe^{57} in nickel as a function of pressure. Error flags are indicated on single points.

The value of the isomer shift at 1 atmosphere relative to stainless steel is +0.146±.04 mm/sec. It is noted that the pressure variation of the isomer shift for Fe^{57} in nickel is about half the value observed for Fe^{57} in iron, while the compressibilities of iron and nickel are approximately the same magnitude.[5]

IV. DISCUSSION

In order to understand the pressure dependence of the isomer shift of Fe^{57} in nickel, it is worthwhile to digress and review earlier results on Fe^{57} in pure iron metal. The magnitude of the observed isomer shift for Fe^{57} in iron is given by[27]

$$\frac{d(IS)}{d(V/Vo)} = 0.134 \text{ cm/sec.} \tag{5}$$

This value may be attributed wholly to a scaling of the 4s wave function with volume.[27] This assumes that the number of conduction electrons remains constant and they are uniformly compressed upon application of pressure. Resistivity-volume data on iron shows that the positive volume derivative of the resistance may be attributed totally to a change in the electron-lattice interaction, consequently, to an increase in the Debye temperature, the number of conduction electrons remaining constant.[28] However, resistivity data on nickel indicate a somewhat smaller decrease in the resistivity with volume than would be expected on the basis of the electron-lattice interaction.[4] The additional resistance may be caused by a decrease in the number of conduction electrons. An estimate of the magnitude of the decrease in conduction electron density is obtained from magnetic data. The saturation moment, σ_o, of nickel decreases with decreasing volume by an amount given by[3]

$$\frac{d\ln\sigma_o}{d\ln V} = +0.5 \qquad (6)$$

If it is assumed that the decrease in the saturation moment is caused by a transfer of electrons from the conduction band to the unfilled 3d band, the decrease in the conduction electron density is given by

$$\left[\frac{d\ln\,\psi_{4s}(o)^2}{d\ln V}\right]_{4s\rightarrow 3d} = +0.5 \qquad (7)$$

Thus, assuming the remaining conduction electron density to be uniformly compressed, the total change in the conduction electron density is given by

$$\left[\frac{d\ln\,\psi_{4s}(o)^2}{d\ln V}\right]_{\text{Total}} = -0.5 \qquad (8)$$

The volume variation of the isomer shift is then given by

$$\frac{d(IS)}{d(V/Vo)} \approx 0.07\ \text{cm/sec.} \qquad (9)$$

This result is in agreement with the experimental result, 0.0789 cm/sec. Considering the assumptions made in this calculation, the agreement with experiment may be fortuitous. In any case, there appears to be a decrease in the 4s electron density which partially counteracts the increase in total s-electron density with compression. Within the experimental error, the isomer shift showed no anomalous behavior at 10 kbars.

The initial increase in the magnitude of the internal field of Fe^{57} in nickel with pressure is in agreement with the increase in the field at Ni^{61} nuclei in nickel. This result further confirms the importance of the host lattice in determining the pressure dependence of the internal field. The observed peak in the internal field at 10 kbars is unexplainable at this time, however, compressibility and resistivity data on pure nickel indicate that the peak may be characteristic of nickel and not the Fe^{57}-nickel system. A similar peak is observed at approximately 75 kbars for the internal field at Fe^{57} in cobalt.[8] Also, on the basis of NMR results, Anderson has suggested the possibility of a maximum in the Curie temperature of cobalt.[29] The pressure dependence of the internal field may be used to estimate the variation of the Curie temperature with pressure.[29] Since the internal field is approximately proportional to the magnetization, the temperature dependence of the field may be estimated by the Bloch $T^{3/2}$ law, which describes the temperature variation of the magnetization well below the Curie point.[1] Using the reported value of dln H/dP for nickel given earlier, the calculated initial increase in the Cure temperature is 0.37°K/kbar compared with an observed value of 0.35°K/kbar. This example illustrates a useful application of high pressure Mössbauer data in solid state physics. The observed peak in H at 10 kbars suggests the possibility of a maximum in the Curie temperature of nickel at 10 kbars.

Although the results given above indicate the importance of the host lattice in high pressure Mössbauer studies, more data are required on pure nickel before we can be certain that the observed effects are not characteristic of the Fe^{57}-nickel system.

V. CONCLUSIONS

The above results illustrate the usefulness of the Mössbauer effect in understanding the coupling of nuclear parameters to the bulk properties of materials. The techniques applied in this work are easily applicable to other Mössbauer experiments. Several experiments are of direct interest with respect to the above results. First, further measurements of the bulk properties of nickel are required from 1 atmosphere to 20 kbars. These data might answer the question of the observed anomalies at 10 kbars. Second, high-pressure Mössbauer measurements of Fe^{57} in other materials such as cobalt with emphasis on the low pressure region are required in order to further confirm the importance of the host lattice in determining the volume dependence of the internal magnetic field and isomer shift.

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