Internal Field of Fe^{57} in Nickel from 77°K to the Curie Point*

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The internal field of very dilute Fe^{57} impurities in nickel has been measured from 77°K to 0.99 T_c. The temperature dependence of the field is not the same as that of the magnetization, the discrepancy reaching 15% at intermediate temperatures. Correction of both magnetization and internal field to constant volume increases the divergence. Over the entire experimental temperature range, the internal field can be represented by a Brillouin function of the form proposed by Jaccarino, Walker, and Wertheim for Mn^{55} in iron, indicating quasi-independent localized impurity moments. The empirical exchange field between Fe impurities and the Ni host is larger than the field between Ni ions, in contrast to the relatively weaker coupling of Mn in Fe. Therefore, the conditions for quasi-independent localized moments seem to be fulfilled for the case of the substantially stronger, as well as the weaker, couplings, in accord with a prediction of Callen, Hone, and Heeger.

I. INTRODUCTION

THE Zeeman splitting of Mössbauer gamma rays from nuclei in ferromagnets has been used as a gauge of the magnetization of the bulk material. In studies of Fe^{57} in iron from low temperatures to the Curie point[1,2] it was found that the hyperfine field of the Fe^{57} is approximately proportional to the magnetization over the entire ferromagnetic range. Similar findings of proportionality have been obtained by nuclear magnetic resonance studies of many other pure materials, such as Ni^{61} in nickel[3] over a temperature range well below T_c. The proportionality is understood to arise primarily from the polarization of the s electrons of the core by the outer d electrons of the atom,[4] although there may be additional positive or negative contributions by the polarization of conduction electrons. Deviations from proportionality may be caused by the thermal excitation of electrons within a band[5] and by thermal expansion[6] but their combined influence is usually not more than a few percent. Recently, however, significant deviations from proportionality have been found. Bennett and Streever[7] found that the resonant frequency of Co^{59} in nickel-rich Ni-Co has a significantly weaker temperature dependence than the host magnetization over the range $0.1<T/T_c<0.7$. Koi, Tsujimura, and Hihara[8] studied an alloy of Mn^{55} in Fe from $T/T_c=0.1$ to 0.6, finding that the Mn^{55} frequency has a temperature coefficient more than three times that of the magnetization, and has a slightly sigmoid shape. Jaccarino, Walker, and Wertheim[9] pointed out that the unusual temperature dependence of the Mn^{55} frequency can be fitted by a Brillouin function of the host magnetization and the temperature. In terms of the reduced field $h=H(T)/H(O)$ and the reduced magnetization $m=M(T)/M(O)$, the equation can be written in the form

$$h=B_J(\zeta T_c m/T), \tag{1}$$

where B_J is the Brillouin function for spin J, and ζ is an empirical constant involving the magnitude of the localized moment and the strength of its interaction with the magnetization. The explanation offered for the success of the molecular-field expression is made in terms of a locally large density of states at the impurity, due to the exchange field between the impurity and the host being weaker than between host ions. Callen, Hone, and Heeger[10] predict that similar local enhancements in the density of states can be caused by localized spin deviations which are coupled either strongly or weakly to the host magnetization.

We find that Fe^{57} impurities in Ni also exhibit quasi-independent local moment behavior, having a temperature dependence that can be closely described by Eq. (1) over the range of temperature from 77°K to within a few degrees of the Curie point. A detailed examination of the critical region is described in a separate communication.[11]

II. EXPERIMENTAL METHOD

Three sources were prepared from 0.001 in. thick nickel foils having quoted purity better than 99.99%. Co^{57} was introduced by drying premium grade $Co^{57}Cl_2$ on the surface of the foil and reducing it in purified hydrogen for $\frac{1}{2}$ h at 1000°C. After several flushes of

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[1] D. E. Nagle, H. Frauenfelder, R. D. Taylor, and D. R. Cochran, Phys. Rev. Letters **5**, 364 (1960).
[2] R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. **128**, 2207 (1962).
[3] R. L. Streever, Jr. and L. H. Bennett, Phys. Rev. **131**, 2000 (1963).
[4] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).
[5] G. B. Benedek, *Magnetic Resonance at High Pressure* (Interscience Publishers, Inc., New York, 1963), p. 21.
[6] C. Robert and J. M. Winter, Compt. Rend. **250**, 3831 (1960).
[7] L. H. Bennett and R. L. Streever, Jr., J. Appl. Phys. **33**, 1093S (1962).
[8] Y. Koi, A. Tsujimura, and T. Hihara, J. Phys. Soc. Japan **19**, 1493 (1964).
[9] V. Jaccarino, L. R. Walker, and G. K. Wertheim, Phys. Rev. Letters **13**, 752 (1964).
[10] H. B. Callen, D. Hone, and A. Heeger, Phys. Letters **17**, 233 (1965).
[11] D. G. Howard, B. D. Dunlap, and J. G. Dash, Phys. Rev. Letters **15**, 628 (1965).

helium to reduce the concentration of dissolved H, the activity was diffused for an additional ½ h in He atmosphere at the same temperature. We estimate that the maximum local concentration of Co^{57} and Fe^{57} is 0.01 at.%, with the average being less than one-tenth as much.

The sources were mounted in a small vacuum oven designed to provide good temperature uniformity. In order to stabilize the temperature, the signal from a chromel-alumel thermocouple was amplified, compared with a mercury cell, and the difference signal applied to the base of a power transistor which controlled the power in the control heater. The sample temperature was measured by an independent thermocouple, and could be maintained constant to within 0.5°C for 8 to 10 h. Both thermocouples were calibrated at the melting points of Sn and Pb.

Internal fields were measured from Doppler velocity spectra obtained with a multichannel Mössbauer spectrometer described previously.[12]

III. EXPERIMENTAL RESULTS

Spectra were obtained at temperatures from 80°K to the critical region and above the Curie point. The appearance of the spectrum was normal at all temperatures, showing no unusual changes in line shapes or relative intensities. In particular, there was no evidence of mixed spectra near the Curie point, such as the 7-line patterns found by Preston, Hanna, and Heberle[2] near the transition temperature of iron, and ascribed by them to inhomogeneities and thermal gradients within their sample. In our best sample the normal 6-line pattern was maintained at all temperatures for which the outer lines could be fully resolved, $T \leq 0.975 T_c$. This source showed lines of nearly natural width when fully resolved or when the source was held above T_c, the resonance width being 0.21 mm full width at half-maximum when obtained with a thin absorber of natural iron. Most measurements, however, were made with single line absorbers of stainless steel or potassium ferrocyanide, which gave appreciably wider combined linewidths. The spectrometer was calibrated with a Co^{57}-Cu source and a thin absorber of natural iron, using the internal field of Fe^{57} in iron measured by Preston, Hanna, and Heberle.[2] Our value for the internal field of Fe^{57} in Ni at 0°K is 280±5 kOe, which agrees with previous measurements.[13] We determined H_0 by extrapolation from the measured H at 77°K, using the same factor 0.995 as for M/M_0 at this temperature.[14,15] In Fig. 1 we show the data in the form of reduced internal field as a function of the reduced

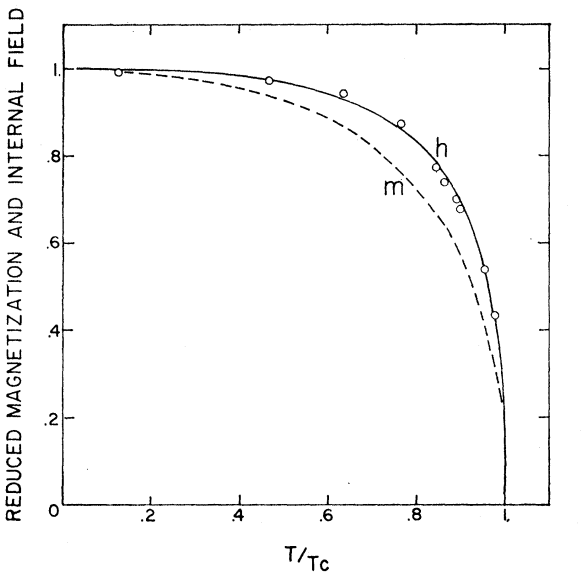

FIG. 1. Temperature dependences of the internal field of Fe^{57} in Ni, the magnetization m of Ni, and the field h calculated according to the molecular field Eq. (1), with $\zeta = 2.6$. Magnetization and field curves are corrected to constant volume, as discussed in the text.

temperature. The value of T_c is taken as 629.4°K, as determined from a study of the critical region.[11]

In contrast to the behavior of Mn^{55} impurities in Fe, the reduced field lies above the reduced magnetization, similar to the case of Co^{59} in Ni-Co. In the region of maximum deviation, near $T/T_c = 0.9$, the reduced field is approximately 15% above the reduced magnetization.

We find that the internal field can be described by a molecular field type of expression, as Eq. (1), over the entire experimental temperature range. In applying Eq. (1) to the data, we chose $J = \frac{3}{2}$ in accord with an assumed $g = 2$ and the moment $2.8\mu_B$ of Fe in Fe-Ni alloys measured by neutron scattering.[16] This spin value also gave a distinctly better over-all fit than either $J = 1$ or 2. The calculated field, based on values of the magnetization at constant pressure,[14] provides reasonable agreement with the data if we choose the value $\zeta = 2.3$; the rms deviation is 2.5%, slightly more than the experimental scatter in h.

The optimum value of ζ is increased when the magnetization and internal field are corrected to constant volume. These corrections can be made in terms of the compressibility, thermal expansion coefficient, and the pressure coefficients of the magnetization and internal field.[5] The pressure coefficient of magnetization of Ni and dilute Fe-Ni alloys is negative,[17] which causes the magnetization at constant volume to be lower by a maximum of about 2% in the region of $0.9T_c$. Although

[12] R. M. Housley, J. G. Dash, and R. H. Nussbaum, Phys. Rev. **136**, A464 (1964).
[13] G. K. Wertheim and J. H. Wernick, Phys. Rev. **123**, 755 (1961).
[14] P. Weiss and R. Forrer, Ann. Phys. (Paris) **5**, 153 (1926).
[15] K. L. Hunt, Proc. Roy. Soc. (London) **A216**, 103 (1953).
[16] G. Low and M. Collins, J. Appl. Phys. **34**, 1195 (1963).
[17] E. I. Kondorskii and V. L. Sedov, Zh. Eksperim. i Teor Fiz. **38**, 773 (1960) [English transl.: Soviet Phys.—JETP **11**, 561 (1960)].

TABLE I. The pressure dependence of internal field H_i of nuclei in Fe-rich and Ni-rich alloys.

Nucleus	Host	$d(\ln H_i)/dP$ (kg/cm^2)$^{-1}$
Ni^{61}	Ni	$+ 8.81\pm0.18\times10^{-7}$ [a]
Co^{59}	Ni	$+13.8 \pm0.5 \times10^{-7}$ [a]
Co^{59}	Fe	$+ 1.6 \times10^{-7}$ [b]
Cu^{63}	Fe	$- 3.0 \times10^{-7}$ [b]
Fe^{57}	Fe	$- 1.6 \times10^{-7}$ [c]

[a] See Ref. 18.
[b] See Ref. 19.
[c] See Ref. 20.

the pressure coefficient of Fe in Ni is not known, it appears that an approximate correction can be based on the coefficient of Co^{59} in Ni, which has been measured.[18–20] The validity of such a substitution seems to be indicated by the dominant influence of the ferromagnetic host on the pressure coefficients of various transition-metal ions in Fe and Ni. In Table I these measurements are listed: There is a distinct grouping of coefficients according to the host. Therefore, we have estimated the correction of the internal field of Fe^{57} in Ni by using the coefficient of Co^{59} in Ni. This raises the internal field above the constant pressure values, in the opposite direction to the revision of the magnetization curve. Correcting both magnetization and internal field to constant volume increases the divergence between their temperature dependences by 50%. The change is reflected in the parameter ζ yielding the best fit between Eq. (1) and the data, being increased from 2.3 to 2.6. The agreement between the calculated curve and the constant-volume data is now the same as was obtained with $\zeta=2.3$ and the uncorrected data. In Fig. 1 we show the constant-volume magnetization and field data and the calculated field according to Eq. (1).

IV. DISCUSSION

The qualitative shape of the field versus temperature curve of Fe in Ni is similar to a classic Brillouin function, and is much less distinctive than the behavior of Mn^{55} in Fe. The difference is reflected in their values of ζ: for Mn^{55} in Fe, $\zeta=0.75$.[9] For ζ smaller than unity, the calculated field tends to be both lower than the magnetization and s shaped, with a final rise toward $h=1$ at low temperatures. When the parameter is larger than 1 as in our samples, the field simply rises toward saturation more quickly as the temperature falls below T_c. An interpretation[9] of ζ was given in terms of a significantly weaker exchange field between the impurity atom and the host than between the host ions. The weaker coupling was considered to be a necessary condition for the sharp resonant impurity state that leads to a quasi-independent local moment. If the association between ζ and the relative magnitudes of impurity-host and host atom exchange fields is taken as a basis, then the exchange field between Fe impurities and Ni host ions is considerably greater than the field between the Ni ions. Therefore, the present case seems to confirm the theory[10] that the molecular field model is also a good approximation of the internal field when the coupling between impurities and the host are significantly stronger than the interactions between the ions of the host.

Jaccarino *et al.* suggest[9] that their value $\zeta<1$ may be correlated with the reduction in average moment caused by adding Mn to Fe: in the dilute range, $d\mu/dc = -2.11\mu_B$ per Mn impurity atom.[21] The present results are consistent with the suggestion: for Fe in Ni, there is an increase of about $2.5\mu_B$ per impurity.[22]

Although we found Eq. (1) adequate to describe the data, we also compared the experimental results with a two-constant equation which might indicate the contribution of conduction-electron polarization. The equation tried is

$$h=\alpha B_J(\zeta T_c m/T)+(1-\alpha)m, \qquad (2)$$

where α is the fraction of field due to the quasi-independent moment, and $(1-\alpha)$ is the nonlocal contribution. There is good agreement with the constant-volume results for a range of ζ and α from $\zeta=2.6$; $\alpha=1$ to $\zeta=3.3$; $\alpha=0.5$. Therefore it appears that the success of Eq. (1) should not be taken as evidence that conduction-electron polarization does not actually make important contributions to the total field. The uncertainty in α, together with the estimated uncertainty in the correction for thermal expansion, indicate that the value of the relative coupling parameter be taken as $\zeta=2.8\pm0.5$.

[18] L. H. Bennett, J. Appl. Phys. **36**, 942S (1965).
[19] T. Kushida, A. H. Siever, V. Koi, and A. Tsujimura, J. Appl. Phys. Suppl. **33**, 1079 (1962).
[20] G. Benedek and J. Armstrong, J. Appl. Phys. **32**, 106S (1961).
[21] A. Arrott and J. E. Noakes, in *Iron and Its Dilute Solid Solutions*, edited by C. W. Spencer and F. E. Werner (Interscience Publishers, Inc., New York, 1963), p. 81.
[22] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), p. 111.