

Nuclear Relaxation of ^{59}Co in Ferromagnetic Ni

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Nuclear magnetic relaxation of ^{59}Co in an alloy of 0.5-at.% Co in Ni has been measured at 4.2 °K with externally applied magnetic fields of up to 12 kG and at 77 and 300 °K with applied fields of up to about 5 kG. The signal recovery following saturation is found to be complicated by the presence of a non-nuclear component which appears with large numbers of saturating pulses. By keeping the number of saturating pulses relatively small we have been able to minimize this effect and obtain accurate values of T_1 . T_1T increases with applied field from a zero-field value of about 0.023 sec °K to a high-field value of about 0.065 sec °K at 12 kG. The high-field relaxation rate is found to be in approximate agreement with a relaxation rate obtained from recent nuclear-orientation studies. Assuming that the high-field relaxation is due to d -orbital interaction, we find, from a comparison of the relaxation rate with that in Ni, that the d -electron density of states at the Fermi level at the Co atom is nearly the same as that at the Ni.

I. INTRODUCTION

In a recent paper¹ we reported on studies of nuclear relaxation times for ^{55}Mn and ^{59}Co in dilute Ni-based alloys, and for ^{61}Ni in Ni metal. The studies were carried out at 4.2 °K, 77 °K, and at room temperature using an externally applied field of about 6 kG. The longitudinal relaxation times T_1 were studied using the saturation method. With small numbers of saturating pulses, relatively short relaxation times were obtained at each temperature, T_1 being of the same order of magnitude as the stimulated-echo decay times. With larger numbers of saturating pulses much longer values of T_1 were obtained. Both the longer as well as the shorter set of relaxation times satisfied roughly the relation $T_1T = \text{const.}$

In the case of ^{59}Co in Ni the value of T_1T based on the short relaxation times was found to be approximately consistent with a value of T_1T obtained from nuclear-orientation studies² of ^{60}Co in Ni, suggesting the longer relaxation times might be non-nuclear. We have carried out some additional studies of the ^{59}Co -in-Ni relaxation which clearly indicate that these longer relaxation times are in fact non-nuclear in origin. These studies are reported in the present paper. By minimizing the non-nuclear relaxation effects we have been able to obtain nuclear relaxation times for ^{59}Co in Ni at 4.2 °K as a function of externally applied magnetic fields up to 12 kG. Experimental results are presented in Sec. II and discussed in Sec. III, where they are compared with results from nuclear-orientation studies.^{2,3} From the observed T_1 a value for the density of states at the Fermi level for Co in Ni is obtained.

II. EXPERIMENTAL

A. Apparatus

The apparatus was basically the same as that

which was described in our previous paper. At the ^{59}Co -in-Ni frequency, however, we found that higher rf power levels could be obtained by placing the sample in the coil of a conventional tank circuit (as opposed to the more complicated tuned circuits needed at higher frequencies). With the Arenberg pulsed oscillator at full power, an rf magnetic field of about 15 G could be obtained across the sample coil.

B. Samples

Some studies were made using the 10–20- μ -sized 0.5-at.% Co-in-Ni powders studied previously. As previously, we studied both the unannealed powders and powders which were annealed for about 2 h in vacuum at 600 °C. The powder samples were sealed in a glass tube into which helium was admitted to act as an exchange gas at 4.2 °K.

In order to improve the thermal contact at 4.2 °K some new samples were prepared by mixing the metal powders in about equal proportions with an epoxy. It was previously observed that the alloy powers were rodlike in shape and seemed to line up in an applied field. Consequently, the samples were placed in a magnetic field of several kG during the several hours that it took the epoxy to set. The resulting samples were permanently aligned and oriented themselves freely along the direction of an applied dc field.

C. Results

1. Preliminary Discussion of Linewidth, Field Shifts, etc.

Most of the studies reported in the present paper were carried out on the epoxy samples at 77 and 4.2 °K. The zero-field frequencies for ^{59}Co in Ni at various temperatures were listed previously. As discussed previously, on application of an external field the resonance shifted to lower frequency. A plot of resonance frequency versus

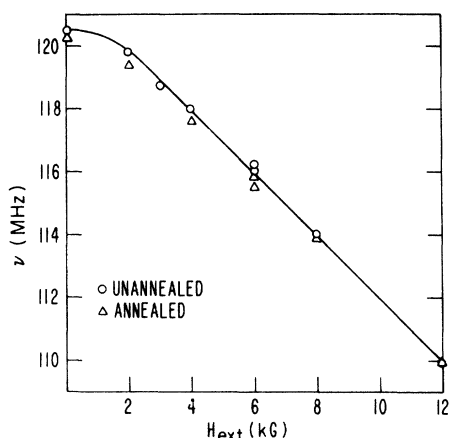


FIG. 1. ^{59}Co resonance frequency versus external field at 4.2°K for 0.5-at.% Co in Ni epoxy samples.

field at 4.2°K is shown in Fig. 1. We see that in fields above about 2 kG the frequency shifted linearly with applied field, indicating that the observed signals were from nuclei in domains. From Fig. 1 one can obtain a demagnetizing field of about 1.5 kG. This is somewhat less than the value expected for a spherical Ni particle, the smaller value probably being a consequence of the rodlike nature of the particles. In applied fields the lines were relatively narrow. At 6 kG the half-signal linewidth obtained with the unannealed epoxy sample was about 2 MHz at 4.2°K .

With an applied field the best echo signal was obtained with two equal $\pi/2$ pulses about $2.5 \mu\text{sec}$ long. With this pulse width the rf level at which the echo maximized increased with increasing applied field owing to the decrease in rotational enhancement factor. At 4.2°K (using the unannealed alloy) the echo signal maximized at an rf level of about 10 G, with an applied field of 12 kG. From the $\pi/2$ condition one can calculate an rf enhancement factor of about 10 at this field. This is in good agreement with an enhancement of 10 which one calculates from the ratio of the hyperfine field to applied field and confirms the fact that the observed signals are from nuclei in domains.

2. Continuous Resonances

In addition to the nuclear resonances a nearly continuous distribution of strong resonance lines was observed with the powder samples. At 77 and 4.2°K these resonances were observed from 80 to 160 MHz. Since the continuous resonances had T_2 's of a few μsec , much shorter than the nuclear T_2 's, they could be easily distinguished from the nuclear signals and could be effectively eliminated from the nuclear signals simply by observing the nuclear echoes at longer times. Furthermore, the continuous resonances exhibited no stimulated

echo.

We found that the continuous resonances could be observed in the frequency range around 100 MHz in various Ni-based alloys (Pt in Ni, Mn in Ni, etc.) and could also be observed in unannealed pure Ni with a somewhat weaker intensity. The continuous resonances were found to maximize with an applied field of about 4 kG. We found that while the continuous resonances could be observed easily in the powder samples they were completely absent in the epoxy samples.

The continuous resonances are probably the same as those observed in lithium ferrite and Ni by Stauss and Rubinstein.⁴ These authors suggested the continuous resonances might be due to ferromagnetic resonance modes or domain walls. Ogawa and Smit⁵ suggest the continuous resonances arise from powder vibrations excited by the rf magnetic field. This would be consistent with their absence in the epoxy samples.

3. Preliminary Relaxation Studies with an External Field of 4 kG

Preliminary relaxation time studies were carried out at 77°K with an applied field of 4 kG using the annealed epoxy samples. Using the saturation method we found that with as few as 3 saturating pulses the recovery following saturation was exponential (over 2 log cycles) with a T_1 of 0.6 msec. With more saturating pulses a longer-time component of about 2 msec appeared in the relaxation. With 50 saturating pulses the 2 msec component represented about $\frac{1}{3}$ of the total relaxation. This is shown in Fig. 2. Similar results were obtained with the unannealed sample except that for small numbers of pulses the 2 msec decay became a larger fraction of the total relaxation, and with more pulses even longer relaxation times began to appear. Essentially the same results were obtained with the powder samples on the nuclear line but

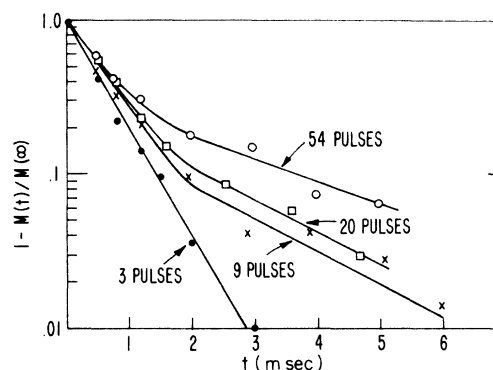


FIG. 2. Relaxation following saturation at 77°K with an applied field of 4 kG, obtained with the annealed epoxy sample.

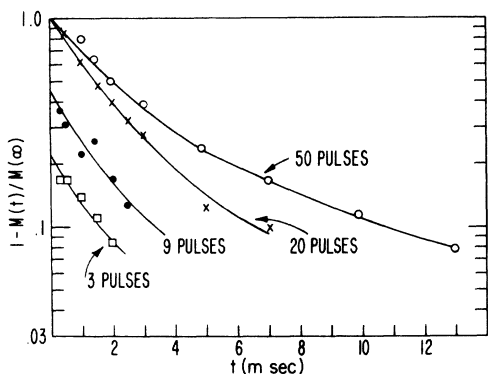


FIG. 3. Relaxation following saturation at 77 °K with an applied field of 6 kG, obtained at 130 MHz (off the nuclear line) with the unannealed powder sample.

with these samples we were also able to monitor the relaxation of the non-nuclear signal at a frequency of 130 MHz (well off the nuclear line). The recovery of the non-nuclear signal following saturation at 130 MHz is shown in Fig. 3. This signal is seen to exhibit the same "apparent" relaxation time as exhibited by the nuclear signal, clearly indicating that the relaxation times of 2 msec and longer are non-nuclear in origin.

Assuming $T_1 T$ to be constant we would expect from the 0.6-msec time at 77 °K to observe a T_1 of about 11 msec at 4.2 °K with the same applied field. In our previous saturation studies at 4.2 °K carried out on the unannealed powder samples we found nonexponential relaxation. The initial relaxation times were of the order of 10–20 msec, while the final relaxation times were about 600 msec. (See Fig. 1 of Ref 1.) In view of the 77 °K results these longer times are evidently non-nuclear and are possibly related to the non-nuclear times observed at 77 °K. In order to verify this we studied the recovery of the electronic signal at 4.2 °K at a frequency of about 145 MHz (well away from the nuclear line) using the unannealed powder sample. With 50 saturating pulses we observed a fast initial relaxation of about 1 msec followed by a longer final relaxation of about 500 msec time which was observed by Chornik⁶ and ourselves¹ in unannealed Ni at 4.2 °K. This longer clear and it likely has the same origin as the 400 msec time which was observed by Chornik⁶ and ourselves¹ in annealed Ni at 4.2 °K. This longer time was not observed at all in the annealed Ni. In the Co-in-Ni samples we have been able to observe it in both annealed as well as unannealed samples, but the relative amount of the longer-time component is weaker in the annealed samples.

In an effort to minimize the non-nuclear effects we carried out saturation studies at 4.2 °K using the epoxy samples. The saturating pulse widths

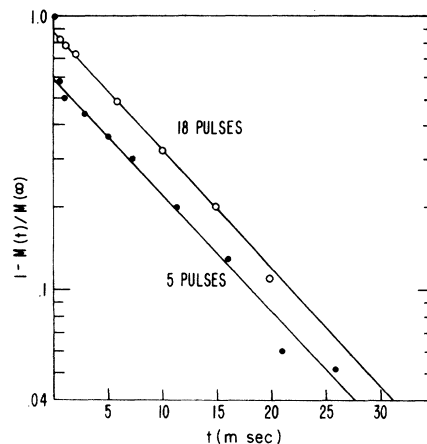


FIG. 4. ^{59}Co nuclear relaxation following saturation at 4.2 °K with an applied field of 4 kG, using the annealed epoxy sample.

were made equal to those of the sampling pulses and the number of saturating pulses were limited to the range between 5 and 20. Under these conditions nearly exponential relaxation was obtained with little trace of the longer times. A typical result is shown in Fig. 4. T_1 was about 11 msec and nearly independent of the number of saturating pulses. The rapid initial relaxation has been observed previously⁷ in the relaxation of ^{63}Cu in Ni.

4. Field Dependence Studies at 4.2 °K

The longitudinal relaxation times were studied at 4.2 °K with applied fields up to 12 kG using the saturation method with about 20 saturating pulses. Results obtained using the annealed and unannealed

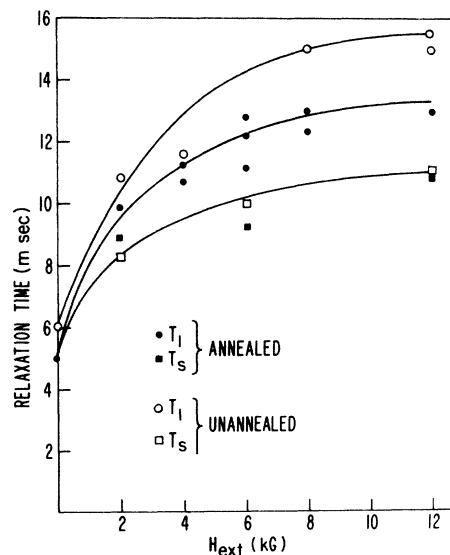


FIG. 5. External field dependence of T_s and T_1 at 4.2 °K.

epoxy samples are shown in Fig. 5. We see that T_1 increases with applied field up to about 12 kG, where the curves appear to be leveling off. Up to this field T_1 is evidently being limited by the presence of pinned domain walls. We see that T_1 is about 20% higher in the unannealed sample at high fields. The annealed sample took longer to mix and may have set up partially before it was placed in the magnetic field. Consequently, it may not be as well oriented as the unannealed sample, which could explain the shorter T_1 .

We also studied the stimulated-echo decay times T_s at 4.2 °K using three $\pi/2$ pulses with a 10- μ sec separation between the exciting pulses. With this pulse separation the spin diffusion contribution to T_s was largely eliminated. The T_s curves were nonexponential. T_s values obtained from the decays at long times are plotted in Fig. 5. We found that T_s was shorter than T_1 and was nearly the same in annealed and unannealed samples. The difference between T_1 and T_s at high fields is similar to that found previously⁹ for ⁵⁹Co in Fe.

We also studied T_2 at 4.2 °K. T_2 was about 1.0 msec at 12 kG and about 0.55 msec in zero field. The field dependence was nearly the same as that for T_s . T_2 was nearly the same in annealed and unannealed samples.

5. Field Dependence at 77 and 300 °K

Studies of T_1 were also carried out at 77 and at 300 °K with applied fields up to about 7 kG (using the epoxy samples). Relatively few saturating pulses (between 6 and 12) were used to avoid the non-nuclear relaxation effects. Over this range of applied fields T_1T was found to be the same (for a given sample) at 300 and 77 °K as at 4.2 °K, within the experimental error.

In Table I we compare at 5.6 kG the values of T_1 , T_s , and T_2 found in the unannealed epoxy sample at various temperatures. At 300 and 77 °K we have used T_2 values obtained previously with the powder sample. We see that both T_1T and T_sT are nearly independent of temperature and T_sT is about $\frac{2}{3} T_1T$ at each temperature. Except for the difference in T_1 which we have already noted the relaxation times were nearly the same in the unannealed sample.

III. DISCUSSION

A. Discussion of T_1 at High Fields

From the T_1 obtained in the unannealed sample at 4.2 °K and 12 kG one can calculate a T_1T of 0.065 sec °K. From this one obtains a normalized relaxation rate $R = (\gamma_n^2 T_1 T)^{-1} \times 10^7$ [sec G² °K⁻¹] of about 3.92. It is of interest to compare our high-field relaxation rate with that obtained from nuclear orientation studies of ⁶⁰Co in Ni. The nuclear-orientation experiments are usually carried

TABLE I. Summary of relaxations times observed at 5.6 kG. All results were obtained with the unannealed epoxy samples except for the T_s studies at 77 and 300 °K, where the powder samples were used.

Temperature (°K)	T_1 (msec)	T_s (msec)	T_2 (msec)
300	0.20	0.14	0.03
77	0.78	0.53	0.05
4.2	14	10	0.95

out on single-crystal foils (with small amounts of ⁶⁰Co) so that magnetic saturation is achieved with relatively low applied fields. Consequently, we would expect the nuclear-orientation studies to yield relaxation rates in agreement with our high-field value. From the nuclear-orientation studies of Ref. 2 a value for T_1T of 0.5 sec °K for ⁶⁰Co in Ni is deduced, corresponding to an R of about 1.55. More recent nuclear-orientation studies³ give a value for T_1T of 0.25 sec °K, corresponding to an R of about 3.10. This value is in reasonably good agreement with our value of 3.92 if one considers that our value of T_1T may be somewhat less than the limiting high-field value.

It should be pointed out that for Co-in-Co metal good agreement is obtained between nuclear-orientation³ and NMR studies⁹ of T_1 . Similarly, as we pointed out in our previous paper,¹ in the case of Co in Fe good agreement is also obtained between the NMR results⁹ and the nuclear-orientation results of Ref. 2.

The high-field relaxation rate should be the intrinsic one for nuclei in the domains. The dominant contribution to the relaxation should be from the orbital interaction with the d electrons. If we consider that the spin-up d band is filled then the orbital relaxation rate can be written simply as¹⁰

$$R_{\text{orb}} = \frac{2}{5} h k_B [H_{\text{orb}} N_{d\downarrow}(E_F)]^2 [1 - (1 - c)^2] \times 10^7 \quad (1)$$

where $H_{\text{orb}} = 2\mu_B \langle r^{-3} \rangle$ is the orbital hyperfine field per unit orbital angular momentum, $N_{d\downarrow}(E_F)$ is the density of spin-down states at the Fermi level, and c is a parameter indicating the degree of t_{2g} character at the impurity site.

For Ni Chornik⁶ has obtained an experimental relaxation rate R_{expt} of 8.4 (based on a T_1 of 52 msec at 4.2 °K), which is in good agreement with a calculated orbital rate of 6.5. Taking $R_{\text{orb}} \approx R_{\text{expt}}$, we obtain $R_{\text{orb}}(\text{Ni})/R_{\text{orb}}(\text{Co in Ni}) \approx 2.1$. We can assume, as has been done in a recent discussion¹¹ of relaxation times in Ni- and Co-based alloys, that $H_{\text{orb}}(\text{Ni})/H_{\text{orb}}(\text{Co in Ni}) \approx 1.6$. Then using Eq. (1) with $c = 1$ (corresponding to equal weights of t_{2g} and e_g orbitals), we obtain $N_{d\downarrow}(E_F, \text{Co in Ni})/N_{d\downarrow}(E_F, \text{Ni}) = 1.1$. This is essentially the result obtained in Ref. 11 using the Co-in-Ni relaxation

rate of 3.0 from the nuclear-orientation studies. This factor of 1.1 can be compared with a value of 0.88, which was calculated in Ref. 11 theoretically from a localized potential model. Consequently, it appears that there is quite satisfactory agreement between theory and experiment at least as far as Co in Ni is concerned.

The relaxation rate for Co in Ni can also be compared with that in Co metal, where a value for R_{expt} of 1.0 has been obtained from ^{59}Co NMR studies⁹ at high fields. If we assume $H_{\text{orb}}(\text{Co in Ni}) = H_{\text{orb}}(\text{Co})$ and take $c = 1$, then we obtain from Eq. (1) $N_d(E_F, \text{Co in Ni})/N_d(E_F, \text{Co}) \approx 2$. This result together with that of the preceding paragraph gives $N_d(E_F, \text{Co})/N_d(E_F, \text{Ni}) \approx 0.55$. This last result is in good agreement with specific-heat data and recent theoretical calculations.¹²

B. Zero-Field Relaxation Rate

For the case of ^{63}Cu in Ni Bancroft⁷ has suggested that the excess relaxation rate for zero field over that at high field is due to a mechanism related to domain walls, whose thermal motion relaxes the nuclei in the wings of the wall. With this mechanism the excess wall relaxation rate R_w should be proportional to $(H_n)^2$, where H_n is the total hyperfine field. R_w is 1.8 for Cu in Ni about 7 for Ni, and about 8 for Co in Ni. The respective values of $(H_n)^2$ are 2.2, 5.6, and $14.4 (\times 10^3) (\text{kG})^2$. The slower observed zero-field relaxation for Co in Ni may be a consequence of a shorter correlation time for the wall motion.

C. Discussion of T_2

Walstedt¹³ has discussed nuclear relaxation times in magnetic metals and alloys and has shown that when quadrupolar broadening is present T_2 will be less than T_1 . If the entire spin-echo signal comes from the $\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition then Walstedt finds $T_1/T_2 = (I + \frac{1}{2})^2$. For ^{59}Co this factor is 16. From Table I we see that T_1/T_2 is 15 at 4.2 and 77 °K and about 7 at 300 °K, suggesting that at 77 and 4.2 °K only the $\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition is contributing to the spin echo. Note that if we consider the Fourier transform of a 3 μsec pulse, the largest excitation would be mainly from a frequency range of the order of 0.1 MHz. Since the quadrupolar splitting could be larger than this (without being resolved) it is quite possible that we are observing mostly the $\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition at low temperatures. At higher temperatures the quadrupolar broadening may be less, so that T_1/T_2 becomes smaller. For the case of Fe^{57} in Fe and ^{195}Pt in Ni, where $I = \frac{1}{2}$,

T_1 is found to be approximately equal to T_2 .

When the quadrupolar splitting is well resolved the longitudinal relaxation will be nonexponential if only the central transition is excited.¹⁴ If, however, the quadrupolar transitions overlap (due to inhomogeneous broadening) then a unique spin temperature will be obtained more rapidly and more nearly exponential relaxation will be observed, even with few saturating pulses. This probably explains why the longitudinal relaxation was generally quite exponential (except at 4.2 °K, where some incomplete saturation was observed).

IV. CONCLUSION

Nuclear-relaxation studies of T_1 which make use of the saturation technique are complicated by the appearance of a non-nuclear component in the signal recovery following saturation. These non-nuclear times are typically 2 to 20 msec at 77 °K, and of the order of several hundred msec at 4.2 °K. They are observed in unannealed Ni as well as in the Ni alloys. Care must be taken in each case to separate the nuclear relaxation from the non-nuclear relaxation.

For ^{59}Co in Ni we find $T_1 T$ to be about 0.065 sec °K, at 12 kG in the unannealed sample. This corresponds to a relaxation rate R of 3.9. This is only slightly larger than the value of 3.0 obtained from the recent nuclear-orientation studies of Ref. 3. The nuclear-orientation studies of Ref. 2 yield a slower relaxation rate of about 1.5. The faster relaxation observed in the NMR studies is evidently due in part at least to the presence of pinned domain walls, which persists up to relatively high fields.

Using a relaxation rate R of 8.4 in pure Ni and a rate of 3.9 for Co in Ni, one finds, assuming d -orbital relaxation, that the d -electron density of states at the Fermi level at the Co atom is nearly the same as that at the Ni.

The situation with respect to ^{55}Mn in Ni which was also discussed in our previous paper¹ is probably similar to that for ^{59}Co in Ni. The longer set of relaxation times which were observed in the unannealed samples (and in the annealed samples at higher temperatures) are likely to be non-nuclear and of the same origin as the longer times observed¹ in Co in Ni, and in the unannealed Ni. The shorter set of relaxation times (see Table II of Ref. 1) corresponding to a high-field $T_1 T$ of about 0.08 sec °K are evidently the nuclear times. More detailed studies of the ^{55}Mn -in-Ni relaxation are planned.

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