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Nuclear Relaxation in Nickel and Nickel Alloys

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Nuclear relaxation times have been measured for ^{55}Mn and ^{59}Co in dilute Ni-based alloys and for ^{61}Ni in Ni metal. Studies have been carried out at 4.2, 77 °K, and at room temperature using an externally applied field of about 6 kG. The signal recovery following saturation is found to be generally nonexponential and to depend on sample annealing. At 4.2 °K, the ^{55}Mn in Ni T_1 for an unannealed sample obtained from the initial recovery is about 13 msec, while that obtained from the final recovery is about 500 msec. For ^{59}Co in Ni at 4.2 °K, the corresponding times are 20 and about 600 msec. By contrast, annealed samples at 4.2 °K exhibit faster and more nearly exponential relaxation with T_1 being 19 msec for ^{55}Mn in Ni and 10–40 msec for ^{59}Co in Ni. Similar behavior is found for the ^{61}Ni relaxation in Ni metal at 4.2 °K, the results being in agreement with those reported by Chornik. Relaxation-time studies have also been carried out for ^{195}Pt in Ni and for ^{55}Mn and ^{59}Co in Fe. The complicated behavior in Ni is discussed and compared with that for the corresponding solutes in Fe.

I. INTRODUCTION

Although studies of nuclear-relaxation times in ferromagnetic metals and dilute alloys can yield detailed information about the electronic structure, in some cases at least the relaxation is quite complicated. A good example is the nuclear relaxation in Ni metal. In a recent paper, Chornik[1] has reported on the nuclear relaxation of Ni^{61} in Ni metal at 4.2 °K. He finds the relaxation in unannealed Ni to be nonexponential at short times but exponential at long times with a long time T_1 of 401 msec. In annealed Ni, however, he finds the relaxation to be exponential with $T_1 = 52$ msec. Chornik concludes that the faster relaxation time measured in the annealed Ni is the intrinsic one and finds reasonably good agreement between the observed relaxation time and that calculated theoretically, taking into account conduction-electron and d-orbital relaxation mechanisms. Chornik points out that there is no obvious explanation for the longer observed relaxation time in the unannealed nickel but suggests it may be related to surface-oxidation effects. Recently we have been studying[2,3] nuclear-relaxation times of the solute nuclei in dilute alloys of Mn and Co in Ni. With respect to annealing we find a similar situation to that in pure Ni. In this paper we discuss the rather complicated relaxation behavior of Ni and Ni alloys and discuss some possible origins of the longer relaxation times observed in the unannealed samples at low temperatures.

Although the main purpose of the present study was to determine the nuclear-relaxation times of ^{55}Mn and ^{59}Co in dilute alloys of Mn and Co in Ni, we have also studied the nuclear relaxation of ^{195}Pt in a dilute alloy of Pt in Ni and have extended Chornik's relaxation-time studies of ^{61}Ni in Ni metal to temperatures above 4.2 °K. We have also studied the nuclear relaxation of ^{55}Mn and ^{59}Co in dilute alloys of Mn and Co in Fe in an effort to help clarify the complicated relaxation behavior observed with the Ni-based alloys. A preliminary account of the ^{59}Co in Fe study has been presented previously.[4]

II. EXPERIMENTAL

A. Relaxation-Time Measurements

Longitudinal relaxation times were measured by first saturating the nuclear magnetization with a comb of rf pulses. The recovery of the magnetization at some later time was determined by applying a pair of closely spaced rf pulses and measuring the amplitude of the resulting spin echo.

The transverse relaxation times T_2 were determined from the echo decays. The stimulated echo decays were also determined by the usual three-pulse sequence. The stimulated echo-decay times T_s were corrected for effects of spin diffusion by plotting the experimental values of $(T_s)^{-1}$ vs τ^2 (τ being the exciting-pulse separation) and extrapolating to $\tau = 0$.

Studies of the ^{61}Ni relaxation in pure Ni and of the solute nuclei in the Ni-based alloys were carried out with applied fields of 5.6 kG or higher. Relaxation times in the Fe alloys were made with applied fields of up to 20 kG.

B. Apparatus

For the resonances which occurred in the range above 225 MHz an Applied Microwave Lab model PG-1K signal source was used to generate the pulses. The necessary pulse sequences were obtained by use of Tektronix-type 162 and 163 units. A Tektronix-type R-116 programmable pulse generator was used to supply the saturating-pulse comb. The rf tuning unit for the range above 225

TABLE I. Zero-field resonance frequencies for ^{61}Ni in pure Ni and for solute nuclei in dilute Fe- and Ni-based alloys.

Nucleus	ν at 300 °K (MHz)	ν at 77 °K (MHz)	ν at 4.2 °K (MHz)	Ref.
^{61}Ni in Ni	26.13	28.26	28.46	a
^{59}Co in Ni	112.3	119.9	120.3	b
^{55}Mn in Ni	310.2	343.7	344.2	c
^{195}Pt in Ni	⋯	309.2	310.9	d
^{59}Co in Fe	279.4	287.7	288.7	e
^{55}Mn in Fe	⋯	238.6	239.1	f

[a] See Ref. 5.
[b] See Ref. 6.
[c] See Ref. 7.
[d] See Ref. 8.
[e] SeeRef. 9.
[f] See Ref. 10.

MHz consisted of a butterfly capacitor with a three- or four-turn sample coil across one end and a single loop across the other end. Additional loops were used to couple to the pulsed oscillator and receiver. Double-stub tuners were placed in the oscillator and receiver lines. For studies in the lower-frequency ranges, an Arenberg pulsed oscillator was used and the sample was placed in the coil of a conventional tank circuit. The rf magnetic field was typically a few gauss. Studies at 77 °K or 4.2 °K were made using nitrogen Dewars or exposed-tip helium Dewars which fitted into the sample coils.

C. Samples

The two principal samples which were studied, 0.8-at.% Mn in Ni and 0.5-at.% Co in Ni, were prepared by an atomization technique, in which the molten ingot is sprayed into a fine powder. The resulting particle size was about 10μ. This procedure is known to leave strains in the alloy, and measurements were made both before and after annealing. The annealing was done for 1 h in vacuum at 600 °C, after which the oven was turned off and the sample was allowed to cool. Alumina powder was mixed with the metal during annealing to prevent sintering and subsequently was magnetically separated.

The pure-Ni powder consisted of high-purity Ni sponge. Other samples discussed here were filed from ingots, and sifted to a particle size less than 50μ. All samples were sealed in a glass tube into which helium was admitted to act as an exchange gas at 4.2 °K.

D. Resonance Frequencies and Linewidths

1. Resonance Frequency and Field Shifts

The zero-field frequencies are listed in Table I. They were found to be in approximate agreement with the results of previous studies.[5-10] In most cases the resonances were followed up from zero field. For the Ni alloys the frequency-vs-applied-field plots became linear in fields in excess of about 2 kG, which represents the demagnetizing field for Ni. For the case of ^{61}Ni in pure nickel the shift of frequency with applied field has been discussed in detail previously.[11] For the Fe alloys the frequency-field plots became linear with fields in excess of about 8 kG, which represents approximately the demagnetizing field of Fe.

2. Linewidths

The linewidths in applied fields were dependent, in general, on temperature, sample annealing, and applied field. At 14 kG and 77 °K the ^{59}Co in the Fe half-signal linewidth was about 6 MHz for the annealed sample, which corresponds to about 6 kG for ^{59}Co. The width probably arises mainly from a distribution in demagnetizing fields since the filed powders could not be expected to be spherical. For ^{59}Co in Ni at 77 °K and 3 kG the width was about 1.4 MHz for the annealed alloy, the narrower width probably being related to a smaller demagnetizing field. For ^{55}Mn in Ni at 4.2 °K and 11 kG the width was about 1.9 MHz, while for ^{195}Pt in Ni the width was 4.1 MHz at the same field and temperature.

For the case of ^{59}Co in Ni, in addition to a relatively narrow central line a broader distribution was observed as well. This broad resonance which had a short T_2 (a few μsec at 4.2 °K) appeared in both annealed as well as unannealed alloys, but at 4.2 °K was stronger in the unannealed samples. At 77 °K at 6 kG the distribution was observed from 80 to 160 MHz. A similar broad distribution was observed at 4.2 °K and a somewhat narrower distribution at 300 °K. All the reported relaxation-time studies were carried out on the central line. At 4.2 °K the long T_2 signal observed in the annealed sample was about a factor of 10 *weaker* than in the unannealed sample at the same point on the line.

3. Other Effects

In the case of ^{55}Mn in Ni another unusual effect was observed. If the echo-producing pulses were applied only once after a long "off time," no echo was produced on the first "shot." The echo built up to a steady value only after several sets of echo-producing pulses were applied and the steady-state echo intensity depended on the repetition frequency. The characteristic time constant involved was of the order of seconds and depended on applied field, temperature, and sample annealing. For Co in Ni this effect was not observed.

E. Results

1. Relaxation Times for ^{55}Mn and ^{59}Co in Nickel

The spin-echo decays and stimulated echo decays were found to be nearly exponential. Values of T_2 and T_s for an applied field of 5.6 kG are listed in

TABLE II. Relaxation times in annealed and unannealed alloys of ^{55}Mn and ^{59}Co in Ni. Values of T_s and T_2 were nearly the same in the unannealed alloys. The applied field was 5.6 kG.

	Temperature	Unannealed T_1 (msec)		Annealed T_1 (msec)		Annealed T_s	Annealed T_2
Alloy	(°K)	Initial	Final	Initial	Final	(msec)	(msec)
0.8-at.% Mn in Ni	300	0.25	12	0.25	11	0.14	0.06
	77	1.4	15	1.2	11	0.66	0.13
	4.2	13	≈500	19	Ref. a	9	1.2
0.5-at.% Co in Ni	300	0.6	4	0.6	3	0.16	0.03
	77	3	23	1.7	5	0.5	0.04
	4.2	20	600	10–40	Ref. a	3.8	0.5
^{61}Ni in Ni	300	0.3	3	Ref. b	Ref. b	Ref. b	Ref. b
	77	2.5	26	Ref. b	Ref. b	Ref. b	Ref. b
	4.2	50[c]	401[c]	50[c]	Ref. a	25[d]	10[c]

[a] No long time observed. [b] Not studied. [c] See Ref. 1. [d] See Ref. 18.

Table II, where T_s has been corrected for the effects of spin diffusion. The values of T_2 and T_s were found to be only slightly dependent on sample annealing.

The T_1 recovery following saturation was in general nonexponential and could usually be characterized by a relatively fast initial relaxation time T_1 (initial) and a longer final relaxation time T_1 (final). The relative amount of long- and short-time decay depended not only on temperature and sample annealing but also on the adjustments of the sampling pulses and saturating-pulse comb.

Consider first the ^{59}Co in Ni signal recovery following saturation at 4.2 °K measured with the unannealed sample. A plot of the recovery for various numbers of saturating pulses is shown in Fig. 1. The sampling pulse widths were 1 μsec, the saturating pulse widths 5 μsec, and the external field was 5.6 kG. We see that the relative amount of long-time decay increased with the number of saturating pulses. Recovery curves obtained at 4.2 °K with 50 saturating pulses for annealed and unannealed alloys are shown in Fig. 2. The annealed alloy exhibited a much faster and more nearly exponential decay. At. 4.2 °K the ^{55}MN in Ni relaxation exhibited a similar behavior, the annealed alloy having a fast and nearly exponential relaxation, and the unannealed alloy showing an appreciable amount of longer-time component.

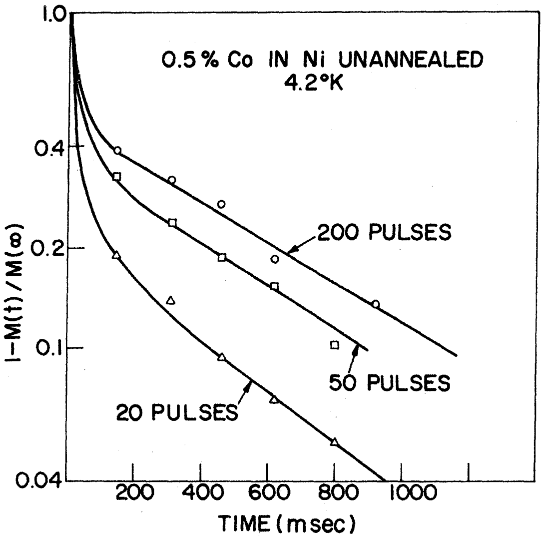

FIG. 1. Longitudinal Co^{59} relaxation for an unannealed alloy of 0.5-at.% Co in Ni in an applied field of 5.6 kG for various numbers of saturating pulses.

For ^{59}Co in Ni the recovery at 77 and 300 °K was nearly exponential for the annealed alloy but with the recovery time dependent on and roughly proportional to the number of saturating pulses. Extrapolating a plot of T_1 vs number of saturating pulses back to zero gave a T_1 of about 0.6 and 1.7 msec at 300 and 77 °K. With 50 saturating pulses the corresponding values were about 3 and 5 msec. Similar results were obtained with the unannealed

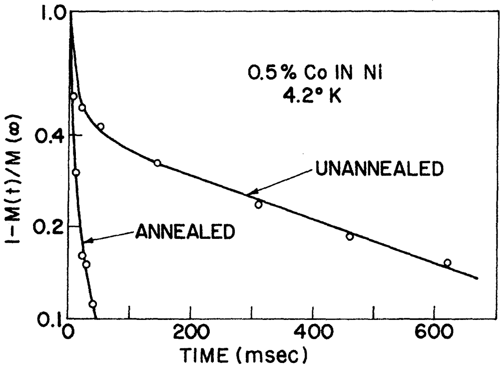

FIG. 2. Longitudinal Co^{59} relaxation for annealed and unannealed alloys of 0.5-at.% Co in Ni in an applied field of 5.6 kG.

alloy at 300 and 77 °K.

At 300 and 77 °K the ^{55}Mn in Ni recovery curves were similar in annealed and unannealed alloys but depended on the sampling pulse width and number of saturating pulses. With sampling pulses about 3 μsec wide and 5–20 saturating pulses of comparable width, the recovery following saturation was nearly exponential and a set of relatively short relaxation times were obtained, T_1 being comparable with T_s. On decreasing the width of the sampling pulses and increasing the number of saturating pulses, the recovery was found to exhibit a long-time component. With 50 saturating pulses and approximately 1-μsec sampling pulses the room-temperature recovery became nearly exponential with a T_1 of about 11 msec in the annealed alloy and nearly the same value in the unannealed alloy. The rather complicated situation is summarized in Table II.

Values of T_1 for Mn in Ni have also been reported by Salamon.[12] His reported T_1's agree with our values of T_s so it appears he assumed $T_s = T_1$ after correction for spin-diffusion effects.

2. *Relaxation Times for ^{61}Ni in Pure Nickel*

We also measured T_1 in the unannealed Ni sponge at 4.2, 77, and 300 °K using the saturation method. Nonexponential recovery curves were observed, the recovery at 4.2 °K being nearly identical to that reported by Chornik. Values of T_1 (initial) and T_1 (final) are listed in Table II.

3. *Relaxation Times for ^{195}Pt in Nickel*

The ^{195}Pt relaxation times in an alloy of 1-at% Pt in nickel were studied at 4.2 and 77 °K with external fields of up to 12 kG. Saturation could be achieved with relatively few saturating pulses and the decay curves were nearly exponential. In fields above about 8 kG, T_1 and T_2 approached limiting high-field values. At 4.2 °K the high-field T_1 was about 12 msec while T_2 was 6.3 msec. At 77 °K the corresponding values were about 1.2 and 0.4 msec. Approximately the same relaxation times were observed in annealed and unannealed samples.

4. *Relaxation Times for ^{59}Co in Iron*

A short preliminary account of the ^{59}Co relaxation times for an alloy of 1-at.% Co in Fe was presented previously. An external field of nearly 20 kG was required to obtain the relaxation times in the high-field limit. Although studies at 77 °K were carried out up to 20 kG, relaxation times at 4.2 °K were made only up to 12 kG. High-field relaxation times at 4.2 and 77 °K are summarized in Table III where the values at 12 kG have been corrected to the high-field limit by multiplying by a factor of 1.2 (see Ref. 4). Although the relaxation at 4.2 °K was nonexponential, unlike the case of Co in Ni, the values of T_s and T_1 were of comparable magnitude at corresponding times. Little if any dependence of relaxation times on sample annealing was found.

5. *Relaxation Times for ^{55}Mn in Fe*

Nuclear-relaxation times of ^{55}Mn in Fe were studied using an *unannealed* alloy of 1-at.% Mn in Fe. At 4.2 °K in an external field of 12.6 kG, T_1 was nonexponential with T_1 (initial) = 22 msec and T_1 (final) = 230 msec. At the same field we found T_2 to be nearly exponential with a value of about 3.1 msec.

III. DISCUSSION

A. Relaxation Times in Ni Alloys

1. *Relaxation Times for ^{59}Co and ^{55}Mn in Ni and ^{61}Ni in Pure Ni*

Before going into any detailed discussion of the relaxation times, note first that the complicated relaxation behavior observed for ^{59}Co and ^{55}Mn in Ni is similar to that for ^{61}Ni in pure nickel. At 4.2 °K the unannealed samples exhibit nonexponential relaxation while the annealed samples exhibit faster and more nearly exponential relaxation.

Two different interpretations of the results appear to be possible. One would be that the longer relaxation times observed in the unannealed samples are the intrinsic ones. A different interpretation would be to assume as Chornik has done for Ni^{61} in pure Ni that the shorter relaxation times observed in the annealed samples are the intrinsic ones. With the latter interpretation one would probably have to conclude that the longer times arise from some type of spurious effect. Since some of the experimental results favor each of these models, we will discuss both in detail.

a. Long-relaxation-time model. The fact that the longer relaxation times satisfy approximately the relation of $T_1 T$ = constant suggests they may be intrinsic. The nonexponential behavior could be understood in terms of a quadrupolar-broadened spectrum. The nonexponential relaxation of a quadrupolar-broadened spectrum has been discussed by Narath[13] and others.[14] When the quadrupolar

TABLE III. Relaxation times for ^{59}Co in a dilute alloy of Co in Fe measured at 4.2 and 77 °K. Relaxation times measured at 12.6 kG have been corrected to high fields by multiplying by a factor of 1.2 (see Ref. 4).

Temperature (°K)	T_2 (msec)	T_s (initial) (msec)	T_1 (initial) (msec)	T_s (final) (msec)	T_1 (final) (msec)
4.2	5	24	30	144	216
77	0.6	0.6	12	8	12

satellites are separated from the main line then the recovery of the spin system following saturation of the central line proceeds nonexponentially. For a spin-$\frac{7}{2}$ system like ^{59}Co the final T_1 could be a factor of 28 longer than the initial decay rate. For a spin-$\frac{5}{2}$ system like ^{55}Mn the corresponding factor is 15, while for a spin-$\frac{3}{2}$ system like ^{61}Ni the factor is 6. The final T_1 would correspond to the T_1 that one would expect for a spin-$\frac{1}{2}$ system. The relative amount of long-time decay would depend on the details of the saturation but would never be more than about 20% for a spin-$\frac{7}{2}$ system in which only the central component was excited directly.

The experimental results (see, for example, Fig. 1) do appear to be consistent with the above model. Note also that the factors T_1 (final)/T_1 (initial) at 4.2 °K are about 30, 38, and 8 for ^{59}Co in Ni, ^{55}Mn in Ni, and ^{61}Ni in Ni, respectively. With the exception of Mn the factors are reasonably close to those that one would expect assuming extreme quadrupolar broadening (well-separated satellites).

If no spin diffusion were present then we would expect T_s(initial) = T_1(initial) with the same model. We see that this is not the case particularly for ^{59}Co in Ni. If, however, pinned walls were present these could affect T_s differently than T_1 through some type of diffusion of the excitation to the walls. Another difficulty with the long-relaxation-time model is in trying to explain the relatively short T_2's. As Walstedt[15] has shown we expect a contribution to T_2' which is given by $T_1/T_2' = (I+\frac{1}{2})^2$. The ratios of T_1(final) to T_2 are considerably greater than these factors.

The fact that long T_1's are observed at room temperature in both annealed and unannealed alloys would also support the long-T_1 model. One would then have to explain, however, why the long T_1's are not observed in the annealed alloys at 4.2 °K. One possibility is that due to a reduced skin depth in annealed alloys at low temperature the rf field is not penetrating completely. Nuclei in the bulk of the sample would not be saturated well and short T_1's would result. This would be consistent with the observation that weak signals were observed at 4.2 °K in the annealed alloys.

b. Short-relaxation-time model. An alternate interpretation would be to assume, as Chornik has done for the case of ^{61}Ni in pure Ni, that the short relaxation times observed in the annealed alloys are the intrinsic ones. One then has the problem of explaining the origin of the longer relaxation times. If one attributes them to sample heating effects of the type observed by Chornik with large numbers of saturating pulses one must still explain why they do not appear in the annealed alloys at 4.2 °K. It may be possible that the rf heating effects are more severe in the unannealed alloys due to a greater rf penetration depth.

Spuriously long relaxation might also arise if nuclei in different parts of the sample were not excited uniformly. If the time required for the excitation to diffuse through the sample were longer than T_1, then this mechanism could lead to spuriously long relaxation. The peculiar dependence of nuclear signal on repetition rate which has been noted previously would also suggest that some effect of this type was occurring. The diffusion time might also depend on the annealing through the change in skin depth with annealing.

If we consider the ^{61}Ni relaxation in pure Ni another factor would tend to favor interpreting the shorter relaxation times as being the intrinsic ones. As Chornik points out, for pure Ni the shorter relaxation time of 50 msec observed in the annealed sample at 4.2 °K leads to a relaxation rate, $R = (\gamma_n^2 T_1 T)^{-1} \times 10^7$, of 8.4 which is in reasonably good agreement with his calculated value of 6.5 based on d-orbital, d-spin, and conduction-electron relaxation mechanisms. The 400-msec relaxation time would lead to a value of R of about 1.0, which is considerably less than the calculated rate.

A similar situation appears to exist for Co in Ni. Recent nuclear-orientation studies[16] of ^{60}Co in Fe and Ni give $T_1 T = 2.6$ sec °K for ^{60}Co in Fe, and $T_1 T = 0.5$ sec °K for ^{60}Co in Ni. Taking into account the different value of γ_n for ^{59}Co and ^{60}Co, we expect $T_1 T$ to be about 0.85 sec °K for ^{59}Co in Fe and 0.16 sec °K for ^{59}Co in Ni. It should be pointed out that in the case of Co in Fe the nuclear-orientation value of $T_1 T$ is in good agreement with the NMR data. For ^{59}Co in Ni then we expect T_1 at 4.2 °K to be about 40 msec, which is consistent with the 40-msec time obtained with the annealed alloy (from the slope of the recovery curve at long times). The shorter times of 0.6 and 1.7 msec obtained at 300 and 77 °K would also be consistent with $T_1 T$ being 0.16 sec °K.

Assuming then that there is no problem with the nuclear-orientation result for Co in Ni, one would have to conclude that the longer T_1's observed for ^{59}Co in Ni are spurious or at least not the intrinsic T_1's. Another possibility must, however, be considered. If the longer times observed in the unannealed alloys were intrinsic ones arising from conduction-electron and d-electron relaxation mechanisms then there is a possibility these relaxation mechanisms might be enhanced in some way in the annealed samples. If a fast relaxation mechanism were operative in the annealed alloys, both nuclear-orientation and NMR studies on annealed alloys would measure short relaxation times times. Nuclear-orientation studies on unannealed alloys would be needed to check out this possibility.

2. ^{195}*Pt in Ni Relaxation*

The relaxation was relatively fast as would be expected from the large s-electron hyperfine coupling constant of Pt. The conduction-electron contribution to the normalized relaxation rate, R_s, will be about 50 times larger for Pt in Ni than that for pure Ni due to the larger s-electron coupling constant.[17] Taking R_s (Ni) to be 0.1 would give an R_s (Pt) of about 5. This can be compared with the experimental rate of about 6. The exponential relaxation would be consistent with the ^{195}Pt spin being $\frac{1}{2}$.

Unfortunately, the ^{195}Pt in Ni results do not establish conclusively the origin of the longer relaxation times observed in pure nickel. If they were intrinsic then the fast s-electron relaxation in Pt would limit them, which could explain the weak dependence of T_1 on annealing for ^{195}Pt in Ni. It may, however, be possible that for some other reason the longer relaxation times are not observed for Pt in Ni.

3. ^{63}*Cu in Ni Relaxation*

The nuclear relaxation of ^{63}Cu in Ni which has been studied by Bancroft[18] appears to be a case where the observed relaxation rate agrees quite well with the calculated one. His alloys were filed and then annealed at 600 °C for $\frac{1}{2}$ h. In view of the pure-Ni results and those for Mn and Co in Ni it would be of interest to know to what extent, if any, T_1 depends on annealing for Cu in Ni.

B. Relaxation Times in Fe Alloys

1. *Relaxation Times for Co*^{59} *in Fe*

In contrast to the complicated situation for ^{59}Co in Ni the nuclear relaxation of ^{59}Co in Fe is relatively simple. First of all there is the good agreement with the nuclear-orientation data already mentioned and with the recent nuclear-resonance studies of Kontani *et al.*[19] Although the T_1 and T_s relaxation curves are both nonexponential at 4.2 °K, at corresponding times T_1 and T_s are of comparable magnitude (see Table III). Finally, little if any dependence of T_1 on sample annealing was found.

The nonexponential behavior of T_s and T_1 and the short value of T_2 suggest the partial excitation of a quadrupolar-broadened spectrum. At 4.2 °K the ratio of T_1 (final)/T_1 (initial) is seen to be about 7. This is considerably less than the factor 28 that one would expect for a case of extreme quadrupolar broadening. For a quadrupolar broadened spectrum we would expect $T_1/T_2' = (I+\frac{1}{2})^2 = 16$ for ^{59}Co according to the Walstedt mechanism. We see that $T_1/T_2 \approx 45$. The additional factor of 3 could reflect some additional anisotropy in the relaxation.

At 77 °K the recovery following saturation was exponential for Co in Fe, suggesting that the quadrupolar broadening might be less or the saturation more effective at this temperature. By contrast T_s was nonexponential at this temperature.

According to the nuclear-orientation results T_1T (Co in Fe)/T_1T (Co in Ni) = 5.2. In Table IV we compare the ^{59}Co in Fe relaxation times at 4.2 °K with those that we would expect for ^{59}Co in Ni if the Co in Ni times were scaled by this factor. We see that the expected Co in Ni times would be consistent with those observed in the annealed alloy if we assume that for Co in Ni, T_s (final) is not being observed.

2. *Relaxation Times for* ^{55}*Mn in Fe*

As mentioned in Sec. II E, at 4.2 °K in an external field of 12.6 kG, T_1 was nonexponential, with T_1 (initial) = 22 msec and T_1 (final) = 230 msec. According to Kontani *et al.*,[19] T_1 (high H) = 27 msec and T_1 (zero H) = 13 msec. Consequently, it appears that the longer T_1 may be spurious or in any case have the same origin as the long T_1 observed in the Ni alloys. Taking the T_1 of 22 msec to be the intrinsic time would give $T_1/T_2 = 7$. Assuming the Mn in Ni T_1 of 19 msec to be the intrinsic one at 4.2 °K would give $T_1/T_2 \approx 16$, which would be of the same magnitude.

IV. CONCLUSION

We have been able to show a similarity between the relaxation of ^{59}Co and ^{55}Mn in Ni and that of ^{61}Ni in pure Ni. A number of results would seem to point to the longer relaxation times being intrinsic ones. Unfortunately, it is difficult to rule out on the basis of the NMR alone the possibility that the longer times are associated with some spurious effect. The fact that the nuclear-orientation relaxation rates for Co in Ni agree with those measured in the annealed alloy would appear to establish the shorter times as being the intrinsic ones in this case. However, as discussed in Sec. III one cannot rule out a real dependence of the relaxation rate on annealing.

From the longer relaxation times observed in the unannealed alloys at 4.2 °K one obtains relaxation rates R for ^{61}Ni in Ni, ^{59}Co in Ni, and ^{55}Mn in Ni of 1.0, 0.1, and 0.1, respectively. From the shorter times observed in the annealed alloys one

TABLE IV. Relaxation times at 4.2 °K for ^{59}Co in a dilute alloy of Co in Fe from Table III are compared with those expected for ^{59}Co in Ni on the basis of the nuclear-orientation studies.

Alloy	T_2 (msec)	T_s(initial) (msec)	T_1(initial) (msec)	T_s(final) (msec)	T_1(final) (msec)
^{59}Co in Fe	5	24	30	144	216
^{59}Co in Ni	1	5	6	28	42

obtains rates of 8.4, 1.5, and 2.9, respectively. As already mentioned, the rate of 8.4 agrees approximately with Chornik's calculated rate for Ni based on *d* orbital, *d*-spin, and conduction-electron relaxation mechanisms. The slower relaxation for the impurity nuclei (which is characteristic of both fast and slow rates) reflects a reduction of *d*-orbital relaxation at the impurity.[4,19]

Additional studies are needed to fully elucidate the complicated relaxation behavior in these alloys and further studies, particularly of Co in Ni, are planned.

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Electron-Spin-Resonance Studies of Mo^{6+}, Mo^{5+}, Mo^{4+}, and Mo^{3+} in Rutile*

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Hydrogen treatment was used to vary the Fermi level in Mo-doped rutile. The stable valence states Mo^{5+} and Mo^{3+} were detected by ESR measurements. The existence of the states Mo^{6+} and Mo^{4+} was inferred from the data. The previously unreported Mo^{3+} resonances can be fit by a spin Hamiltonian $\mathcal{H}=\vec{H}\cdot\overleftrightarrow{g}\cdot\vec{S}+DS_z^2+E(S_x^2-S_y^2)\vec{I}\cdot\overleftrightarrow{A}\cdot\vec{S}$, with $S=3/2$, $g_c=1.94$, $g_{\bar{1}10}=1.97$, $g_{110}=1.95$, $D=5.58$ cm^{-1}, $E=0.99$ cm^{-1}, $A_c=3.83\times10^{-3}$ cm^{-1}, $A_{\bar{1}10}=3.50\times10^{-3}$ cm^{-1}, and $A_{110}=3.56\times10^{-3}$ cm^{-1}. The *z* axis coincides with the crystalline *c* axis.

INTRODUCTION

Several authors[1] have noted changes in ESR line intensities of substitutional ions in rutile as a result of oxidation, reduction, or other treatment of the sample. Johnson and DeFord[2] interpret these changes in terms of the variation of the crystal Fermi energy and associated change of trapping level occupation probability. These authors have worked out the thermodynamics for the case of doping with a donor impurity, such as hydrogen, and have studied the optical-absorption changes of Mo-doped rutile which result from progressive hydrogen doping.

In this paper we discuss the effects of hydrogen doping on the ESR of Mo in rutile, including results for the previously unreported Mo^{3+} state. The ESR of Mo^{5+} substituted for Ti^{4+} in rutile has previously been studied by Kyi[3] and Chang.[4] Faughnan and Kiss[5] have inferred the transient existence of Mo^{6+} in photochromic processes. The stable Mo charge states range from 3+ to 6+. This range corresponds to 180 eV of free-ion ionization energy. It is at first sight surprising that the trapping levels associated with this spread of ionization energy are localized in the 3-eV band gap of rutile. It can be shown[6] that the energetics of the system can be qualitatively explained in terms of a balance between Madelung, ionization, and polarization energy terms.

EXPERIMENTAL RESULTS

The initial experiments were carried out on crystals double doped with Mo and Al. The Al acts