Nuclear Magnetic Resonance in Dilute Ni-Base Alloys

By AKIRA TSUJIMURA

Department of Physics, Faculty of Science,
Shinshu University
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Abstract

The nuclear magnetic resonance (NMR) of impurity nuclei have been observed in Ni-base alloys using a steady state method and a spin echo method. Firstly, measurments of the NMR frequency of the Cu^{63}, Ni^{61}, Co^{59}, Fe^{57} and Mn^{55} nuclei in Ni alloys was measured as a function of temperature in the range from 4.2° K to 550° K, respectively. The temperature dependences of the internal fields are not identical to that of the magnetization of Ni host. The discrepancy depends on the hyperfine constant.

Furthermore, the pressure dependence of their fields at 273° K in the range 1 to 8000 kg/cm² has been measured with the result that the dl_nH_i/dP of Cu^{63}, Ni^{61}, Co^{59} and Mn^{55} nuclei in Ni alloys are 1.66×10^{-7} (kg/cm²)⁻¹, 1.20×10^{-6} (kg/cm²)⁻¹, 1.74×10^{-7} (kg/cm²)⁻¹ and -3.32×10^{-7} (kg/cm²)⁻¹, respectively. It is found that the resonance frequency of the impurity nuclei is not proportional to the bulk magnetization even at constant volume. A brief discussion on mechanisms possible as the source of the exchange interaction is given.

§ 1 Introduction

Since a strong Co^{59} NMR signal had been observed in ferromagnetic f.c.c. cobalt metal[1], NMR technique has been used to investigate the internal field, H_i, which is the magnetic field at the nuclei in ferromagnetic metals, alloys and compunds[2,3]

In particular, high accuracy of this technique enables us to measure very precisely the internal fields at the impurity nuclei as well as the host nuclei in dilute ferromagnetic alloys and gives detailed informations on the electronic structure of alloys.

The internal fields at various impurity nuclei such as Mn^{55}, Fe^{57}, Co^{59}, Ni^{61} and Cu^{63} in ferromagnetic alloys were observed by means of the NMR[2,4,5] and Mössbauer technique[6].

These investigations showed that the internal field at an impurity nucleus in Ni alloys arises from the moment of the impurity atom, if they have the moment, and the moments of the nearest neighbour Ni atoms.   The internal field at the Cu^{63} nucleus is mainly due to the effect of the nearest neighbor Ni atoms.

The temperature dependence of the internal field at Mn^{55}, Fe^{57}, Co^{59} and Ni^{63} nuclei in Ni alloys is measured. The discrepancy is attributed to the fact that the proportionality constant depends slightly on temperature, although it is partly due to the effect of thermal expansion[7].

The purpose of this experiment is to elucidate the temperature and pressure dependence of the internal field at impurity nucleus in ferromagnetic Ni base alloys and to investigate the electronic configurations and the spatial distribution of the magnetization.

The detailed experimental technique and apparatus are described in §2. The temperature and pressure dependences are given in §3.

§2 Sample, Experimental Technique and Apparatus

a) Samples

The samples used in experiment were prepared by the follwing procedur e. A mother alloy which contains about 20 atomic percent metals was prepared from nickel metal of 99.9% purity and metal of the same purity in argon atmosphere in an induction furnace. The samples of a few percent alloy were prepared by the same method from the mother alloy of 20 atomic percent metals. The resulting ingot was ground to powder by a grinder, and was passed through a sieve of 300 mesh. The product was sealed in an evacuated quartz tube and annealed at 450°C for 24 hours.

b) Spectrometers and Pressure Apparatus

The apparatus consists of a spectrometer, a frequency-meter, a high pressure pump and a pressure bomb in which a radio-frequency coil and the sample are enclosed. The NMR signal was observed with a marginal oscillator and a spin echo oscillator.

1) The spectrometer in case of the steady state method

The spectrometer used is a push-pull Colpitts oscillator with a frequency-modulation device. The oscillators are not stopped by the strong absorption of radio-frequency energy due to a ferromagnetic sample of sufficient amount.

The block diagram of the whole measuring system, the circuit diagram and the arrangement of various parts are shown in Fig. 1, Fig. 2 and Fig. 3 respectively. * The frequency modulator consists of a metal foil attached to a 3″ dyna-

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* This spectrometer was constructed as early as 1960 on the suggestion of Professor Y. Kôi.
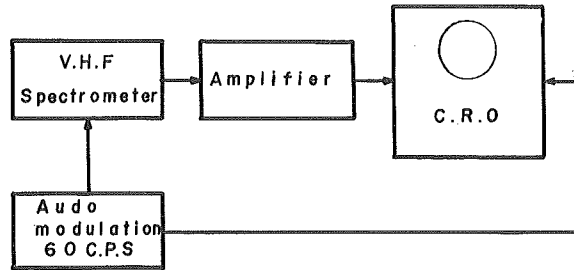
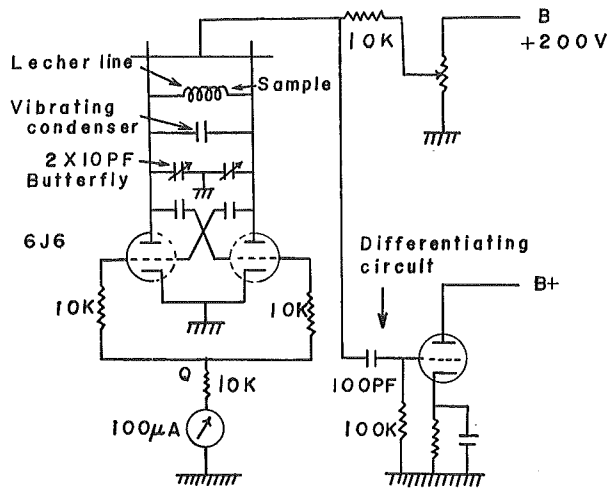**Fig. 1.** Block diagram of the audio modulation and
detection system

Fig. 2. Circuit diagram of the V. H. F. spectrometer
(1) shorting bar   (2) sample coil   (3) vibrating condenser
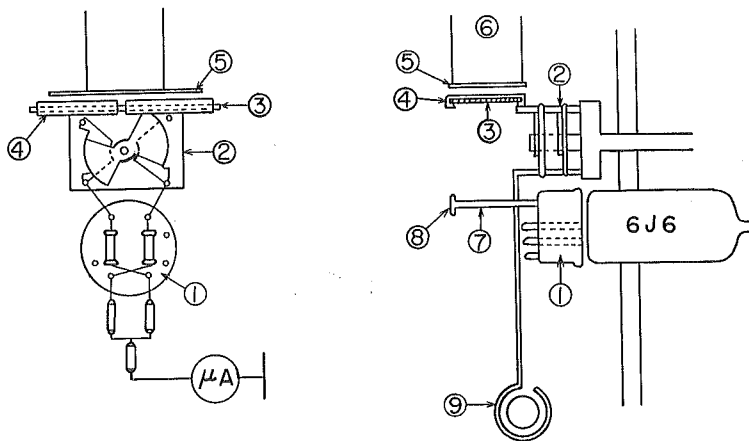

Fig. 3. Arrangement diagram of spectrometer parts
(1) soket   (2) butterfly condenser   (3) mica plate   (4) copper plate
(5) aluminum plate   (6) paper pipe   (7) Lecher line   (8) shorting bar
(9) sample coil

mic speaker and placed near butterfly condenser as shown in Fig. 3. The Lecher-line scheme can be used from 400 Mc/sec down to about 100 Mc/sec. However, in the frequency range below 200 Mc/sec, we can use a coil instead of the Lecher-line; the sample is then placed in the coil. The coil scheme has the advantage that the smaller amount of sample can be treated with; the Lecher-line scheme has the advantage that the oscillation frequency can be changed quite easily. The sensitivity is highest at the condition of marginal oscillation. The osillation level of the spectrometer may be monitored with the grid current microammeter. The plate voltage as low as 50 volts. In this circuit, it is very difficult to change the temperature and pressure at the sample because of too short distance between the sample and the vacuum tube 6J6.

When the sample needs to be at a considerable distance from the spectrometer, it is placed in a sample coil which is inserted between the two plates of the vacuum tube 6J6 through a transmission line of suitable length as shown in Fig. 2.

The out put voltage of the spectrometer contains a voltage change due to the frequency modulation (F-M). This voltage is usually much higher than that from the nuclear resonance, and accordingly makes it impossible for nuclear signal to be displayed on the oscilloscope in spite of its large S/N ratio. The difficulty was overcome by using the following technique. The out put of the spectrometer is fed to the oscilloscope through a differentiating circuit. Since the nuclear signal has a derivative larger compared with the F-M signal, it can be taken out as the first derivative. The differentiating circuit can be considered to be a high-pass filter whose cut off frequency is very high. Then it is natural that the F-M signal is cut off. In some cases where further differentiations are needed, the 2nd or 3rd derivative curve is obtained on the oscilloscope, but the 3rd derivative is the limit because of the S/N ratio.

The resonance line was displayed on a CRO screen and its frequencies was measured by superposing a signal from a heterodyne wave meter on the resonance signal. For the detection of the week resonance line, the super-regenerative spectrometers are usually used because of their simplicity and high sensitivity. The quenching voltage of 500 kc/sec~1.5 Mc/sec is added to Q shown in Fig. 2. However, the super-regenerative scheme seems not to be suitable for the study of line shape and line width, because the line shape depends upon the amplitude and frequency of the quenching voltage.

   2) *The spectrometer in the case of the spin echo method*

The broad signal of NMR can not be detected by the steady state method, therefore the spin echo method is used to search the broad signal.

The brock diagram of apparatus is shown in Fig. 4. In the following, each
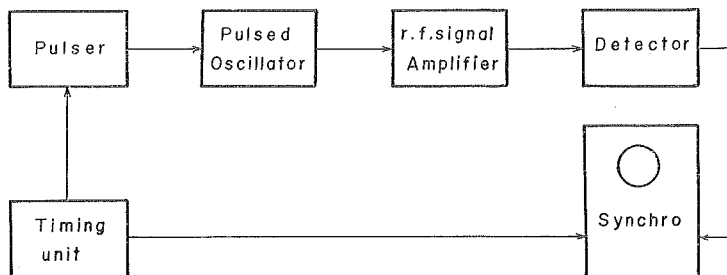
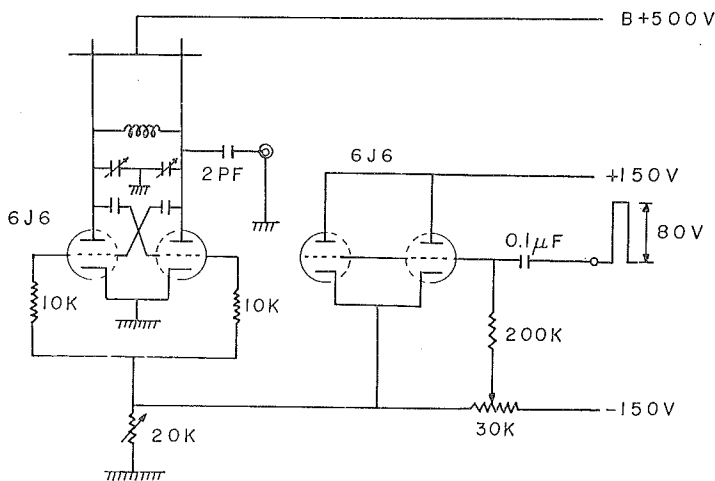Fig. 4. Block diagram of the whole pulse apparatus

Fig. 5. Circuit diagram of the pulsed oscillator

unit of the apparatus is described in detail.

Each element of the timing unit is of usual type to obtain the basic trigger generator which is determine the repetition interval[8].

To obtain the basic trigger signal, a cathode couple astable multivibrator with RC differentiator is employed. The delay circuit which determines the pulse interval is composed of a cathode-coupled monostable multivibrator and a differentiator.

In the mixer unit, the first and second triggers are mixed. They are desired to have a same wave-form. For this reason, the last section in the basic triggered generator is inserted. The pulsers were triggered by the timing unit to create rectangular waves of controllable widths. We have used an electron coupled monostable multivibrator to create short pulses (1μ sec in minimum).

The pulsed oscillator was essentially the same as that for the quadrupole

resonance echo of DAS and HANN[9]). The osillator is the push-pull Colpitts type. The circuit diagram of the pulsed oscillator is shown in Fig. 5.

In order to detect the NMR signal, a signal super-heterodyne method was employed. This method was suitable for searching NMR signal and for following the change of the resonance frequency with variation of the temperature or the pressure. The receivers are broad-band rf amplifiers followed by a diode detector and a cathode follower output. The amplification stages are arranged in maximally flat stagger-triples[10]) and are coupled by means of bifilar transformers which are sluge tuned. The intermediate frequency was chosen as 25 Mc/sec, and the band width of the i.f. amplifier as 4 Mc/sec. The circuit diagram of the receiver is shown in Fig. 6.

3) *Pressure apparatus*

The high-pressure pump was designed by KÔI and constructed under his guidance, and the pump generates hydrostatic pressure up to 10,000 kg/cm². It is similar in structure to the one used by FUKE[11]) when he observed the pressure dependence of nuclear quadrupole resonance.
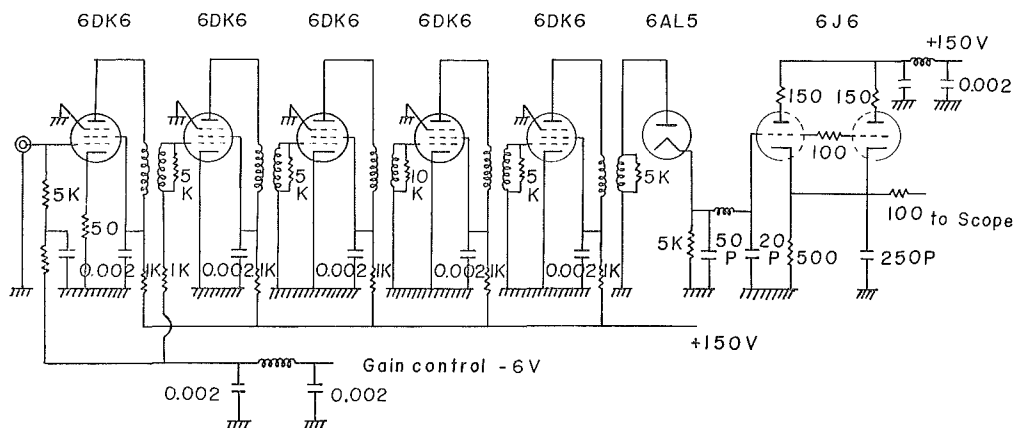

Fig. 6. Circuit diagram of rf signal amplifier

§ 3 Experimental Results and Discussion

The temperature dependence of the NMR frequency of the nuclei in Ni base alloys have been measured in the temperature range between 4.2° K and 550° K. The temperature dependence of the resonance frequency, ν, is expressed empirically as

$$\nu = \nu_0 \ (1 - c\,T^{3/2}) \tag{1}$$

up to 270° K, where c is constant.

The Mn resonance frequency at 4.2° K is 344.9 Mc/sec, which corresponds to an internal field of 326.8 kOe.

The internal field extrapolated to 0° K at Mn^{55}, Fe^{57}, Co^{59}, Ni^{63} and Cu^{63} nuclei in Ni alloys are -327 kOe, -280 kOe, -120 kOe, -75 kOe and -47 kOe, respectivly.

The internal field arises from the hyperfine interaction between the nucleus and both the core and conduction electrons, as has been discussed by MARSHALL[12], and can be written as

$$H_i = A\sigma, \qquad (2)$$

where A is the proportionality constant and represent the hyperfine interaction and σ is the spontaneous magnetization.
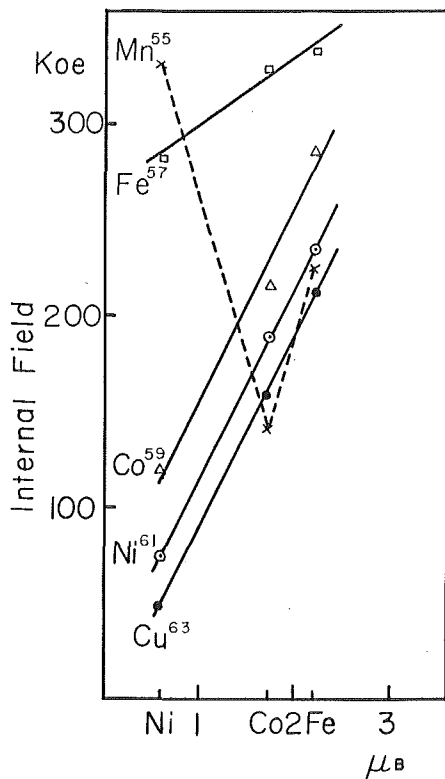

Fig. 7. The internal field at the sites of Cu^{63}, Ni^{61}, Co^{59}, Fe^{57}, and Mn^{55} nuclei vs the effective number of Bohr magneton per atom

Fig. 7 shows the plots of the internal fields at the Cu^{63} nucleus, Ni^{61} nucleus[14], Co^{59} nucleus[15], Fe^{57} nucleus[16], and Mn^{55} nucleus[5] in dilute Ni, Co and Fe alloys against the effective numbers of Bohr magneton per atom.

The field of their nuclei except Mn nucleus is proportional to effective number of Bohr magneton of the host metal. But the field of Mn nucleus is not proportional, because the local moment of Mn in Ni alloy differs very markedly from the moment in Co, Fe alloys. The sign of the field at the impurity nucleus has been determined to be negative[17]. The minus sign means that the field is antiparallel to magnetization of the host. The field at the nucleus of any atom is generally expressed by

$$H_i = a\,\mu_{self} + b\,\bar{\mu} \qquad (3)$$

where H_i is the internal field at any

nucleus, μ self is the moment of the atom in concern, $\bar{\mu}$ is the average moment of alloy, and a and b are the constants.

Probably for the Cu nucleus the first term is vanished or very small and for other kind of nuclei the first term dominates over the second. Then it is natural to assume that the increase of the magnitude of the field from the value 50 kOe at the Cu nucleus to the value 330 kOe at the Mn nucleus is caused by increasing of the local moment.

From the NMR experiment[18], it is concluded that the internal ifeld at Mn^{55} nucleus in Ni alloy arises mainly from the magnetic moment of the parent Mn atom, and the Mn atom is likely to have a magnetic moment of about 3 μ_B, which is in agreement with the results of the magnetization measurements.

The results of the temperature dependence of the resonance frequency at Mn^{55}, Co^{59}, Ni^{61} and Cu^{63} nuclei in Ni alloys and the spontaneous magnetization under constant pressure are shown in Fig. 8, in reduced scale, namely as the ratio ν/ν_0 and σ/σ_0 versus T/T_c, where T_c is the Curie temperature, 630°K, ν_0
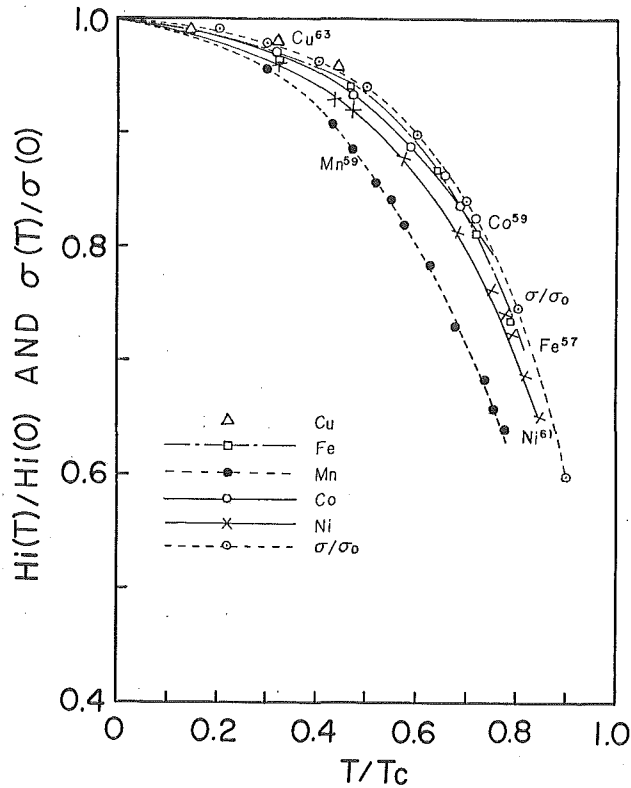
Fig. 8. $H_i(T)/H_i(0)$, σ/σ_0 versus T/T_c of Mn^{55}, Co^{59},
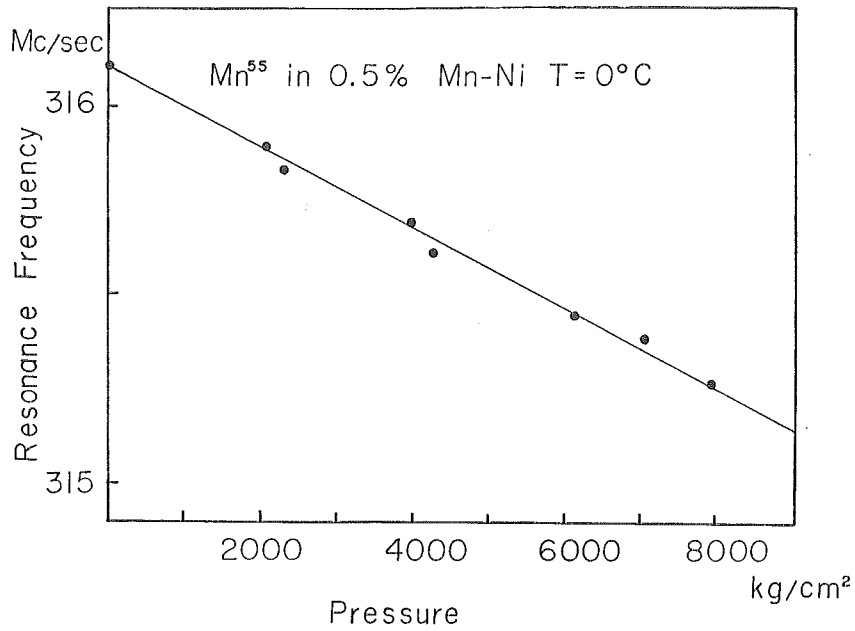Ni^{61}, and Cu^{63} nuclei in Ni alloys

Fig. 9.1. The resonance frequency of the Mn[55] nucleus inNi-0.5at.
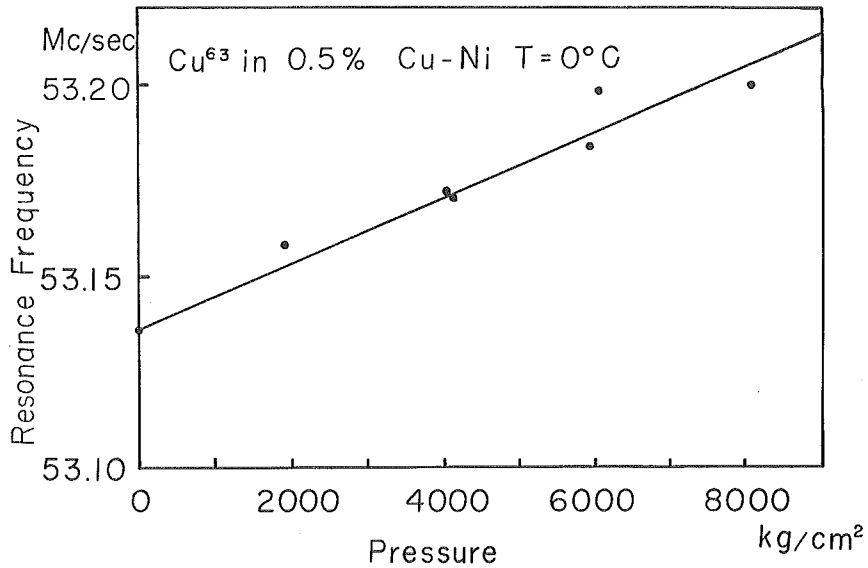% Mn as a function of pressure at 0°C

Fig. 9.2. The resonance frequency of the Cu[63] nucleus in Ni-0.5at.
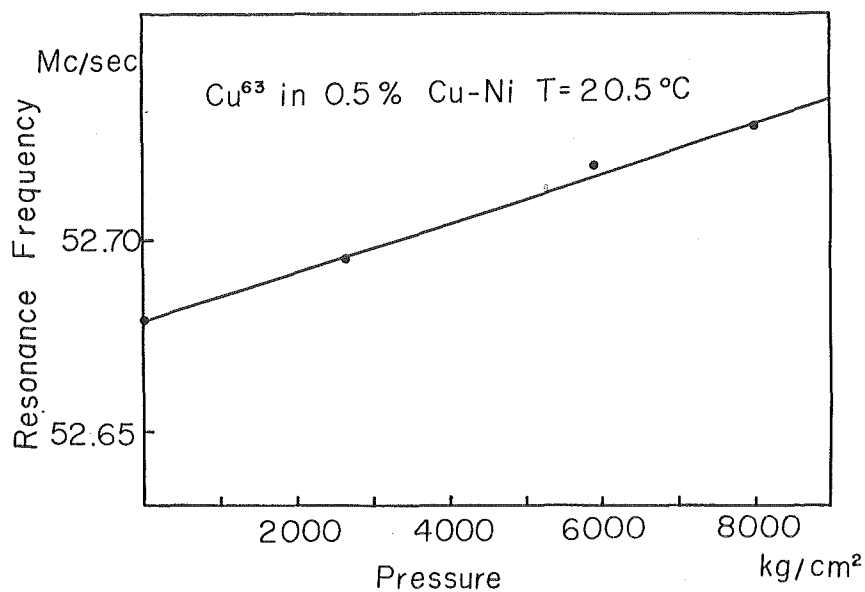% Cu as a function of pressure at 0°C

AKIRA TSUJIMURA

Fig. 9.3. The resonance frequency of the Cu[63] nucleus in Ni-0.5at.
% Cu as a function of pressure at 20.5°C

Fig. 9.4. The resonance frequency of the Co[59] nucleus in Ni-0.5at.
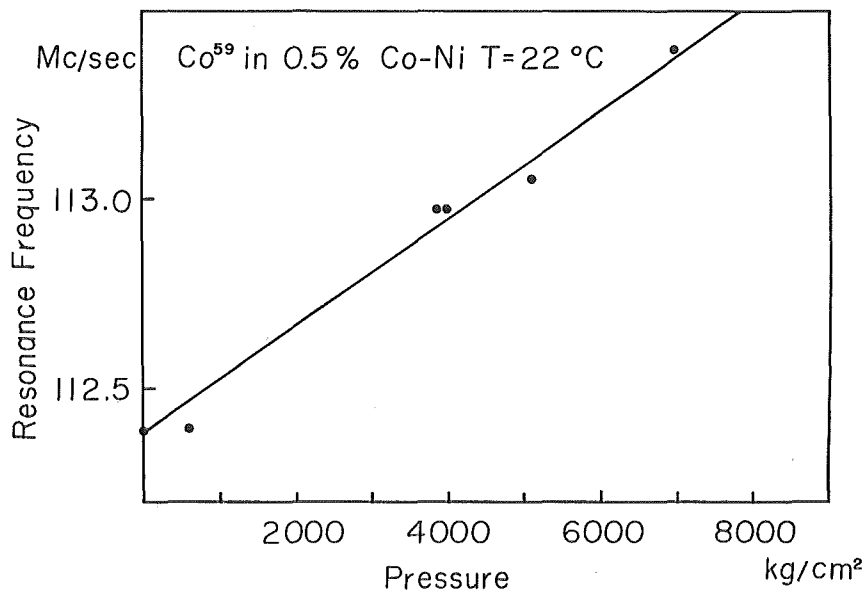% Co as a function of pressure at 22°C

and ∂_0 are the values of ν and ∂ at $0°$ K. ν/ν_0 at the Mn^{55} nucleus decreases with increasing temperature more rapidly than that at Ni^{61} nucleus.

A simillar descrepancy between the temperature dependence of Ni^{61} and Co^{59} resonance frequency in Ni rich Ni-Co alloy was noted by BENETT and STREEVER[4], although the Co resonance frequency drops off more slowly with temperature than the Ni resonance frequency. The pressure dependence of NMR frequency has been measured to see whether this discrepancy between the temperature dependence of the Ni^{61} and the Mn^{55} resonance frequencies in Ni-Mn alloys is caused simply by an *implicit* effect of temperature via thermal expansion or by an *explicit* temperature effect, namely, to see whether or not this discrepancy still exist at constant volume. Measurement of the pressure dependence of the resonance frequency makes this point clear. Therefore, the Mn^{55}, Co^{59} and Cu^{63} resonance frequencies in Ni alloys were measured as a function of pressure.

The Mn^{55} resonance frequency decreases linearly with increasing pressure as shown in Fig. 9. 1.

The resonance frequencies of Co^{59} and Cu^{63} nucleus increase with an increase in pressure as shown in Fig. 9. 2, Fig. 9.3 and Fig. 9.4.

The results are shown in Table 1.

The temperature dependence of resonance frequency is not identical with that of the magnetization under a constant pressure as shown in Fig. 8. It is possible to estimate the value of the difference between $(\partial \nu / \partial T)_V$ and $(\partial \nu / \partial T)_P$ by using the thermodynamic relation

$$(\partial \nu / \partial T)_P = (\partial \nu / \partial T)_V + (\partial \nu / \partial V)_T (\partial V / \partial T)_P \tag{4}$$

i. e.,

$$(\partial \nu / \partial T)_P = (\partial \nu / \partial T)_V - 3\alpha/K(\partial \nu / \partial V)_T \tag{5}$$

Variations in the resonance frequency and the magnetization at constant volume can be calculated by using the values for $(1/\nu)d\nu/dP^{[19]}$ and the value of $1/\sigma \partial \sigma / \partial P^{[20]}$ together with data on the compresibility $K^{[21]}$ and the thermal expantion $\alpha^{[22]}$. For the spontaneous magnetization the values by FONER[23] up to $292°$

Table 1 The pressure dependence of the internal field H_i at
Mn^{55}, Co^{59}, Ni^{61} and Cu^{63} nucleus in Ni alloys

Nucleus	$d\ln H_i/dP$ (kg/cm²)	
Mn^{55} in Ni	-3.32×10^{-7}	at 0°C
Co^{59} in Ni	12.74×10^{-7}	at 22°C
Ni^{61} in Ni	$1.26 \times 10^{-6[19]}$	
Cu^{63} in Ni	1.66×10^{-7}	at 0°C
	1.42×10^{-7}	at 20.5°C

K and the data of WEISS and FONER[24] from $292°$ K to $520°$ K has been used.

There are a definite discrepancy among ν/ν_0 at Mn^{55}, Fe^{57}, Co^{59}, Ni^{61} and Cu^{63} nuclei even at constant volume as seen from Fig. 8. This discrepany is attributed to an intrinsic temperature dependence of A, although it is partly infulenced by the effect of thermal expansion. Recently STREEVER and BENETT[4] showed that A weakly depends on temperature. The qualitative shape of the reduced field versus the reduced temperature curve of the Mn^{55} resonance frequency in Ni-Mn alloy[18] is much less distinctive than the behaviour of that of the Mn^{55} nucleus in Fe-Mn alloy[25].

The vaarition of $H_i\,(T)/H_i\,(0)$ for Mn^{55} nucleus in Ni alloy is more rapid than that of $\sigma\,(T)/\sigma\,(0)$ for Ni host but on the contrary the variation of $H_i\,(T)/H_i\,(0)$ in Ni alloy is slower than that of the reduced magnetization for Ni.

From the above results, it is concluded at least qualitatively that the exchange field between Cu, Co and Fe impurities and Ni host atoms are stronger than the field between the Ni atoms themselves, on the other hand, the exchange field between Mn impurities and Ni host atoms is weaker than the field between the Ni atoms themselves.

Acknoledgement

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