Coordination Chemistry Fundamentals

# Instrumental Analysis of Coordination Compounds

Volume 2

Edited by Hiroki Oshio and Graham N. Newton

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# Instrumental Analysis of Coordination Compounds
Volume 2

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# *Instrumental Analysis of Coordination Compounds*
## *Volume 2*

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# *Preface*

The 1950s are often referred to as the Renaissance of inorganic compounds, yet the true significance of metal complexes was only fully realized in the latter half of the 20th century. Research in metal complexes spans a broad spectrum of topics, from syntheses and reactions to structures and physical properties. The instrumental analysis of metal complexes is critical to the field, and can often lead to the thrilling discovery of unexpected phenomena. The breadth of measurement and analysis techniques that are now available dictate that the coordination chemist should have wide-ranging knowledge of areas such as quantum chemistry, thermodynamics, kinetics, equilibrium theory, analytical chemistry, surface chemistry, and solid-state chemistry, to name but a few. This book not only explains the methods but also the principles of the measurements and the fundamental theory required to ensure that data can be collected and interpreted correctly and the necessary information can be extracted.

We could not measure physical properties in our labs or institutes a half-century ago. First, we booked the instruments and waited for days or weeks for the measurements. Some measurements themselves took several days, but we did not feel it was inconvenient. The data obtained through a combination of time and effort were valuable, and the results made us happy or sometimes disappointed. Nowadays, however, labs and institutes are filled with analytical instruments, from everyday workhorse tools used in every undergraduate lab to advanced developmental pieces of equipment that are rarely used.

Instruments have generally been improved from analog to digital, and anyone can easily obtain data by pressing the START button. However, the more convenient it becomes, the more we are accustomed to always having the data and the less impressed we are. Last century, in a more inconvenient era, we had the time to learn about the measurements while waiting for

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access or data collection to complete. Since measurement data were rarely obtained, we could ponder the obtained spectrum and the sequence of numbers all night long. It is generally believed that "more convenience enriches society," and so the world of instrumental analysis has developed steadily. However, we may sometimes feel, "There is no need to make everything more convenient." We need more time to face the measurements and consider the obtained data.

This book serves as a comprehensive commentary and introduction to instrumental analyses of metal complexes, a valuable resource for all chemists. It covers nearly all the instruments necessary for modern research, meeting the demands of this era. However, it's essential for the reader not to be complacent with this book alone. They should be inspired to strive for a deeper understanding by exploring the more specialized books referenced in this text, fostering a continuous learning mindset.

A deeper understanding will foster intuition and lead to discovery.

Hiroki Oshio and Graham N. Newton

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CHAPTER 1

# *Magnetic Measurement*

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## 1.1 Introduction

Magnetic measurements are now much more familiar to researchers in inorganic and coordination compounds than thermal and electrical resistance measurements. Electrical resistance measurements provide information on the electrical state by the contact method. Whereas magnetic measurements are performed by the non-contact method, they are convenient for evaluating the physical properties of as-synthesized samples. Magnetic measurements give information on the microscopic state of compounds, such as electronic state, structure, and magnetic interactions, as well as the macroscopic state, such as magnetic transition temperature, coercive force, magnetic domain structure, *etc.* Magnetic measurements have also become indispensable in the research fields of nano-sized magnetic materials and superconductors. Recently, magnetic measurements have become more accessible without high operating skills. Commercially available instruments are simultaneously user-friendly and highly sophisticated. However, users can fall into a trap and believe the quantified results without any doubt. It is important to always verify the data accuracy, and sometimes one needs to go back to the calculation process of the obtained data. In this chapter, we introduce basic knowledge of the measurement devices and methods and show some examples of analyzing the magnetic properties of coordination compounds.

Most chemists nowadays use electromagnetic induction style devices or superconducting quantum interference devices (SQUIDs) for magnetic

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measurements. In this chapter, we focus on these measurement methods, divided into **static magnetic measurement (DC measurement)** to detect the magnitude of the magnetic momentum and **alternating current magnetic measurement (AC measurement)** to detect the dynamic magnetic response to periodic external fields. In particular, the AC measurement, being indispensable for evaluating magnetic properties, is introduced in detail.

The DC measurement provides the fundamental magnetic properties of compounds (paramagnetism, diamagnetism, magnetic interactions, *etc.*) as the temperature- and field-dependences of the magnetic susceptibility. It has been easier for chemists to carry out measurements at high cryogenic temperatures and high magnetic fields with the cooperation of physicists so far. In recent years, chemists have been able to work at cryogenic temperatures of 0.5 K and with high magnetic fields of 10 T (tesla) in their laboratories, although it is still difficult to use pulsed high magnetic fields. On the other hand, the AC measurement is an important method to evaluate the dynamic magnetization process, which yield essential data for the magnetic property analysis of single molecule magnets, single ion magnets, single chain magnets, spin qubits, *etc.* The AC measurements are divided into the $10^{-2}$ Hz to 1 kHz range using SQUID and the 10 Hz to 10 kHz range using electromagnetic induction-based devices. The AC magnetic susceptibility data over a wide frequency range have become essential in recent research on nano-sized magnetic materials for magnetic recording media and medical applications. Here, it should be noted that commercially available magnetic measurement devices automatically correct for eddy current effects and calculate the complex magnetic susceptibility, due to the presence of metallic materials in the space where the AC magnetic field is applied. It is essential to understand this point when attempting high-pressure experiments using a pressure cell partly made of metal. The various magnetic measurement methods presented in this chapter are classified into three levels, and their characteristics are compared in Table 1.1.[1,2] The details are explained below.

## 1.2 Static Magnetic Measurement (DC Measurement)

When a substance with magnetic moment $\boldsymbol{m}$ is placed in a magnetic field, the substance creates a new magnetic field called magnetization. The magnetization value ($\boldsymbol{M}$) in response to the uniform and steady (no time variation) static magnetic field ($\boldsymbol{H}$) is called a magnetization curve. Usually, when the magnetic field $\boldsymbol{H}$ is increased from zero, the magnetization $\boldsymbol{M}$, which corresponds to the magnetic moment per unit volume, is proportional to $\boldsymbol{H}$ in the small magnetic field (eqn (1.1)).

$$\boldsymbol{M} = \chi \boldsymbol{H} \tag{1.1}$$

**Table 1.1** Categorization of magnetic measurements.

| Large category | Middle category | Small category | Observed physical quantity | Measurement accuracy [emu] | Feature |
|---|---|---|---|---|---|
| Static (DC) magnetic measurements | Dynamical methods | Magnetic balance | Vertical magnetic force | $10^{-6}$ | Simple electric and mechanical system, zero field measurement is possible |
| | | Magnetic pendulum | Horizontal magnetic force | $10^{-6}$ | No influence of gravity |
| | | Cantilever | Torque | $<10^{-10}$ | High field measurement is possible |
| | | Capacitance method | Vertical magnetic force | $10^{-6}$ | Suitable for low temperature measurement because of small heating |
| | Electromagnetic induction method | Extraction methods | Electromotive force | $10^{-5}$ | Suitable for high field, high pressure, and low temperature |
| | | Sample vibration method | Electromotive force | $10^{-6}$ | Lock-in detection is promising |
| | | Coil vibration method | Electromotive force | | Lock-in detection is promising |
| | SQUID method | DC magnetic method | Magnetic flux | $10^{-8}$ | High accuracy, most conventional method |
| | | Sample vibration method | Magnetic flux | $10^{-8}$ | Lock-in detection is promising |
| | | Coil vibration method | Magnetic flux | $<10^{-9}$ | Lock-in detection is promising |
| Alternating current (AC) magnetic measurements | Electromagnetic induction method | | Electromotive force | $10^{-7}$ | Promising for high frequency measurements |
| | SQUID method | Superconducting magnetic flux transformation | Magnetic flux | $10^{-8}$ | Promising for low frequency measurements |

The slope $\chi$ evaluated within the linear relationship of the $\boldsymbol{M}$ and $\boldsymbol{H}$ values is called the susceptibility or magnetic susceptibility. $\chi$ is usually calculated by dividing $\boldsymbol{M}$ by $\boldsymbol{H}$ in the DC measurements. Here, $\boldsymbol{M}$ includes the contribution from the diamagnetic field due to diamagnetic components. If only the magnetically active elements are to be evaluated using eqn (1.1), a correction for the diamagnetic field is necessary.[3] There are various methods for measuring $\boldsymbol{M}$, unlike AC susceptibility (see Section 1.4); **static magnetic measurements** detect the magnitude of $\boldsymbol{M}$ in a static magnetic field that does not change over time.

Next, the units of the magnetic field should be mentioned. The relationship between the magnetic flux density $\boldsymbol{B}$ and the magnetic field $\boldsymbol{H}$ is as follows.

$$\boldsymbol{B} = \mu_0 \boldsymbol{H} \tag{1.2}$$

Table 1.2 lists units of $\boldsymbol{H}$ and $\boldsymbol{B}$. In the cgs unit system, the unit of $\boldsymbol{H}$ is Oe (oersted) and $\boldsymbol{B}$ is G (gauss). By convention, G is often used as the unit for $\boldsymbol{H}$ in the sense of the value of $\boldsymbol{H}$ corresponding to $\boldsymbol{B}$, based on the assumption that 1 Oe = 1 G from the vacuum permeability $\mu_0 = 1$. In this case, emu (electromagnetic unit) is used as the unit of magnetic susceptibility $\chi$.

In this chapter, the static magnetic measurements (DC methods) are classified into three methods; the mechanical method, which measures the force acting on substances (Section 1.2.1), the electromagnetic induction method, which measures induced electromotive force using electromagnetic induction (Section 1.2.2), and the superconducting quantum interference device (SQUID) method (Section 1.2.3). Some consider the SQUID method, which uses mutual induction in the magnetic flux conversion between the pick-up coil system and the SQUID, to be included in the electromagnetic induction method. But since its characteristics differ from the original electromagnetic induction method, this chapter describes the SQUID method separately from the electromagnetic induction method.

### 1.2.1 Mechanical Method

The mechanical method has been used before the SQUID method became popular. This method measures the magnetic force exerted on a magnetized sample by the non-uniform magnetic field between

**Table 1.2** Magnetic field and magnetic flux density units.

| | Symbol | cgs unit system | Conversion constant (cgs→SI) | SI unit system |
|---|---|---|---|---|
| Magnetic field | $H$ | Oe | $10^3/4\pi$ | $\mathrm{A\,m^{-1}}$ |
| Magnetic flux density | $B$ | G | $10^{-4}$ | T |

the poles of an electromagnet. When a substance with magnetic moment $\boldsymbol{m}$ is placed in a magnetic field $\boldsymbol{H}$, the magnetic energy is $-\boldsymbol{m}\cdot\boldsymbol{H}$. The following equation expresses the force $\boldsymbol{F}$ acting on the magnetic moment.[2]

$$\boldsymbol{F} = -\,\mathrm{grad}(-\boldsymbol{m}\cdot\boldsymbol{H}) \tag{1.3}$$

$$= \boldsymbol{m}\times\mathrm{rot}\,\boldsymbol{H} + \boldsymbol{H}\times\mathrm{rot}\,\boldsymbol{m} + (\boldsymbol{H}\cdot\mathrm{grad})\boldsymbol{m} + (\boldsymbol{m}\cdot\mathrm{grad})\boldsymbol{H} \tag{1.4}$$

Here, all terms on the right-hand side of eqn (1.4) are zero except for the fourth term, assuming no current ($\mathrm{rot}\boldsymbol{H}=0$) and uniformly-magnetized sample, then the following equation is obtained.

$$\boldsymbol{F} = (\boldsymbol{m}\cdot\mathrm{grad})\boldsymbol{H} \tag{1.5}$$

To consider eqn (1.5) in detail, place the sample at the position where the magnetic field gradient is maximum between the poles of the electromagnet (Figure 1.1). In this case, the magnetic field is $\boldsymbol{H}=(H_x, 0, 0)$. If the effect of magnetic anisotropy in the crystal is ignored, the magnetic moment $\boldsymbol{m}$ is directed to the magnetic field direction. That is, $\boldsymbol{m}=(m_x, 0, 0)$. In addition, the relationship $\partial H_x/\partial x = \partial H_y/\partial x = 0$ holds when an electromagnet with symmetrical poles is used. In this case, the force $\boldsymbol{F}$ is expressed by eqn (1.6).

$$\boldsymbol{F} = \left(m_x\frac{\partial H_x}{\partial x}, m_x\frac{\partial H_y}{\partial x}, m_x\frac{\partial H_z}{\partial x}\right) = \left(0, 0, m_x\frac{\partial H_z}{\partial x}\right) \tag{1.6}$$

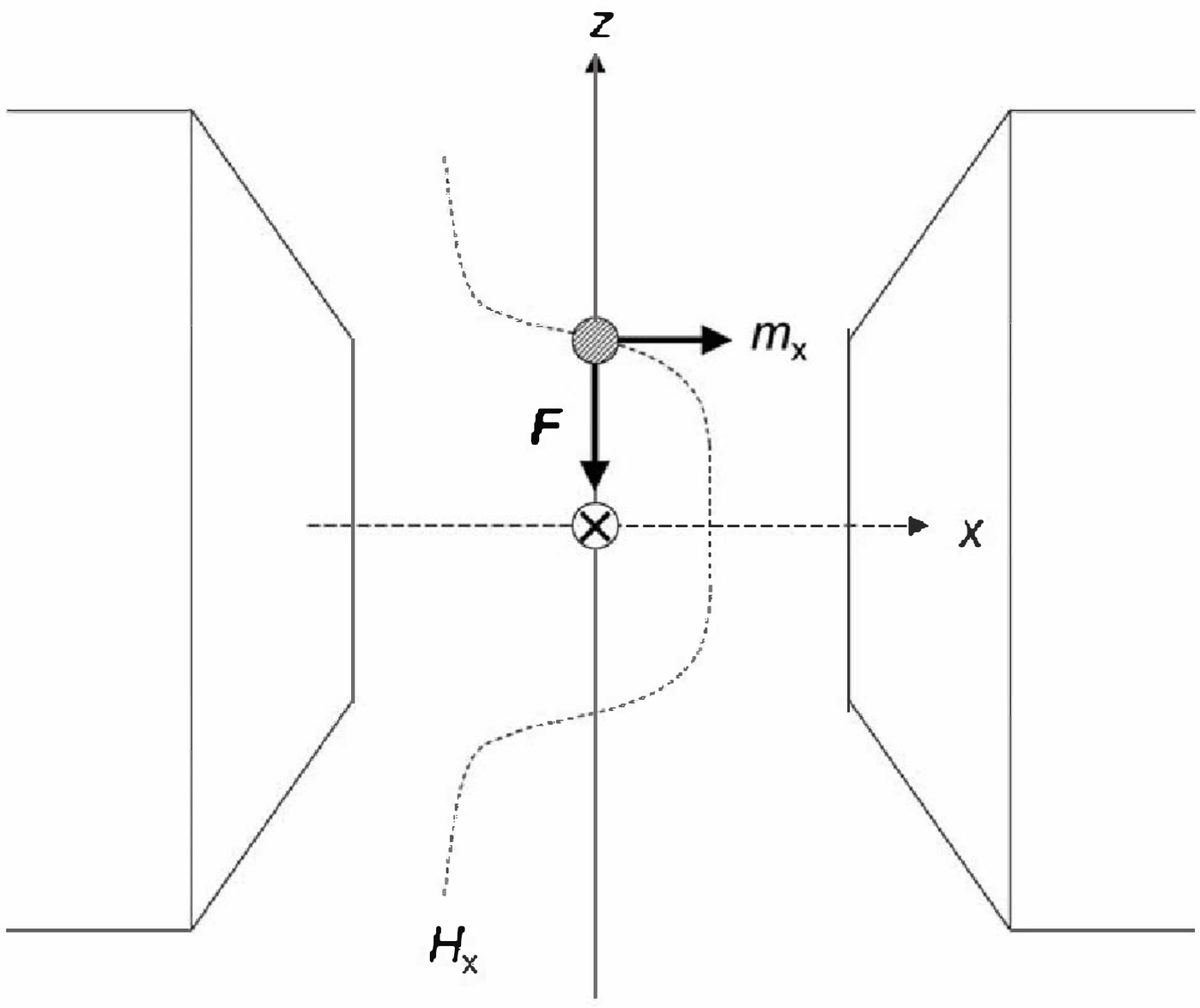


**Figure 1.1** Force $\boldsymbol{F}$ acting on a sample placed in a gradient magnetic field between the poles of an electromagnet.[2]

Here, $\partial H_z/\partial x = \partial H_x/\partial z$ from the condition $\mathrm{rot}\,\boldsymbol{H} = 0$, which leads to eqn (1.7).

$$\boldsymbol{F} = \left(0, 0, m_x \frac{\partial H_x}{\partial z}\right) \tag{1.7}$$

The magnetic moment $\boldsymbol{m}$ can be calculated by measuring the force $\boldsymbol{F}$ acting on the sample placed in a non-uniform magnetic field. For the actual force measurement, we need to keep the sample at the position of the maximum magnetic field gradient, so the zero-detection method, which feeds back a signal proportional to the force, is used. The disadvantage is that the magnetic field of the electromagnet cannot be used effectively because the sample is not located at the position of the maximum magnetic field.

A representative apparatus for mechanical methods is the magnetic balance magnetometer (Faraday method), which uses a balance for weighing. As shown in Figure 1.2, a sample is suspended between the poles of electromagnets, and feedback coils are placed on the other side, in which a permanent magnet is suspended. When a current is applied to the feedback coil to keep the balance, the magnitude of $\boldsymbol{F}$ is measured from the magnitude of the current. Since we measure forces in the direction of gravity here, we need to compensate for the contribution of additional forces except for magnetic forces.

On the other hand, pendulum-type magnetometers measure the force acting in the horizontal plane, so only the magnetic force is measured. In both cases, the magnetic moment $\boldsymbol{m}$ can be evaluated by measuring the magnetic force using a balance. While magnetic balances have good sensitivity, they are not suitable for measurement in strong magnetic fields due to their instability against lateral shaking. Recently, strain gauges (commonly known as load cells) have been used for force detection. Among them, a small cantilever can be applicable for measurement under a strong magnetic field.

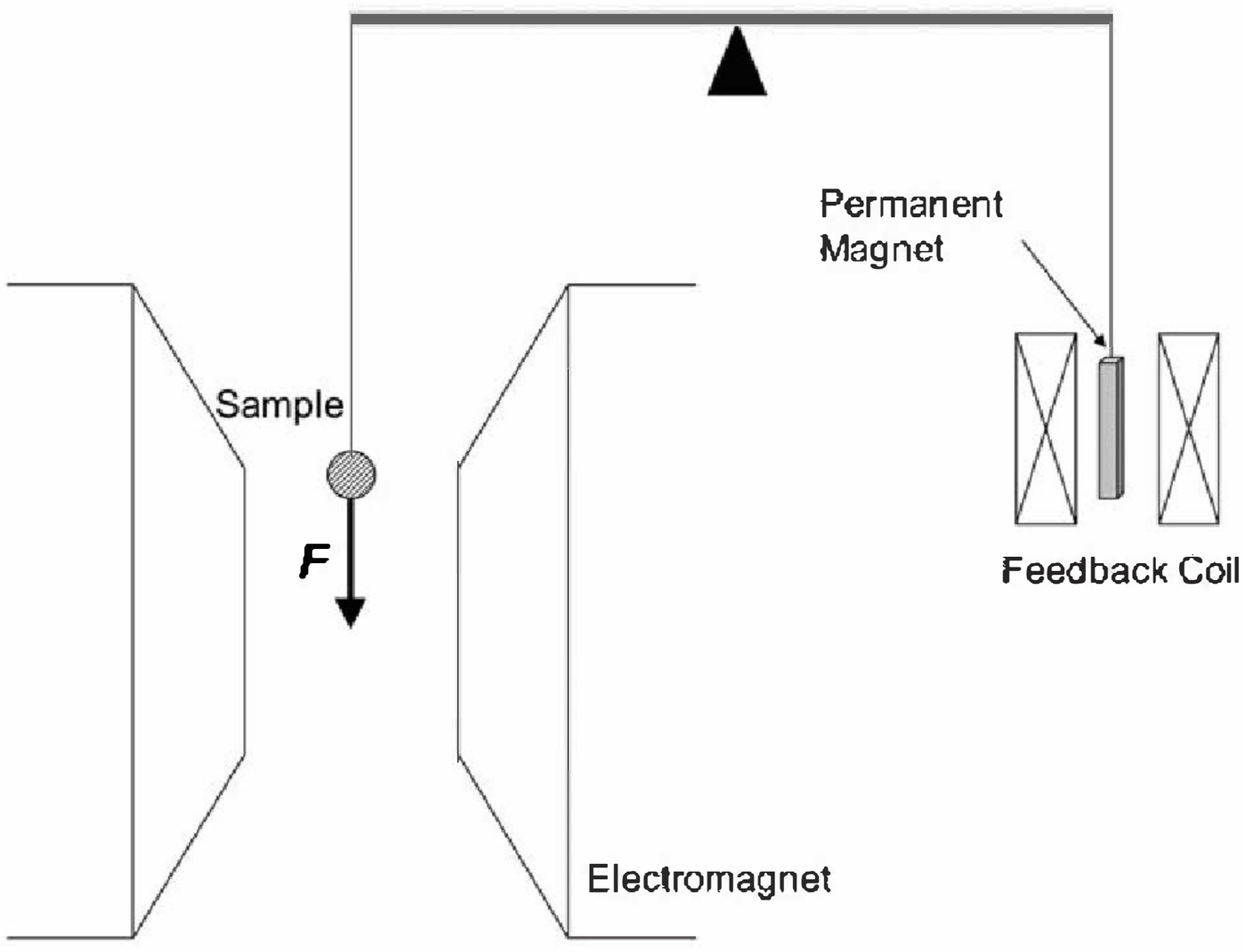


**Figure 1.2** Schematic of a Faraday balance magnetometer.[2]

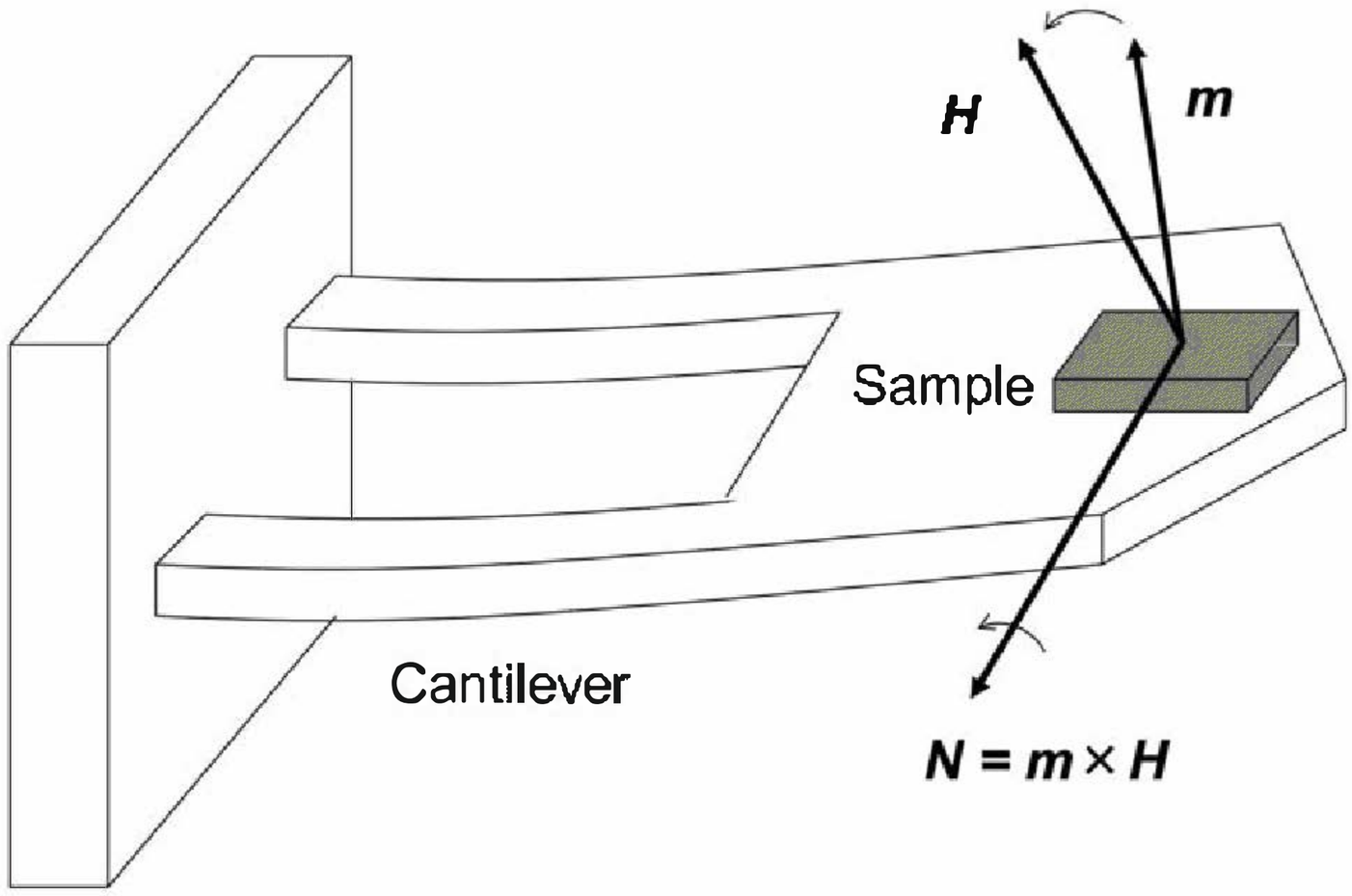


**Figure 1.3** Principle of magnetic measurement using cantilevers.[4]

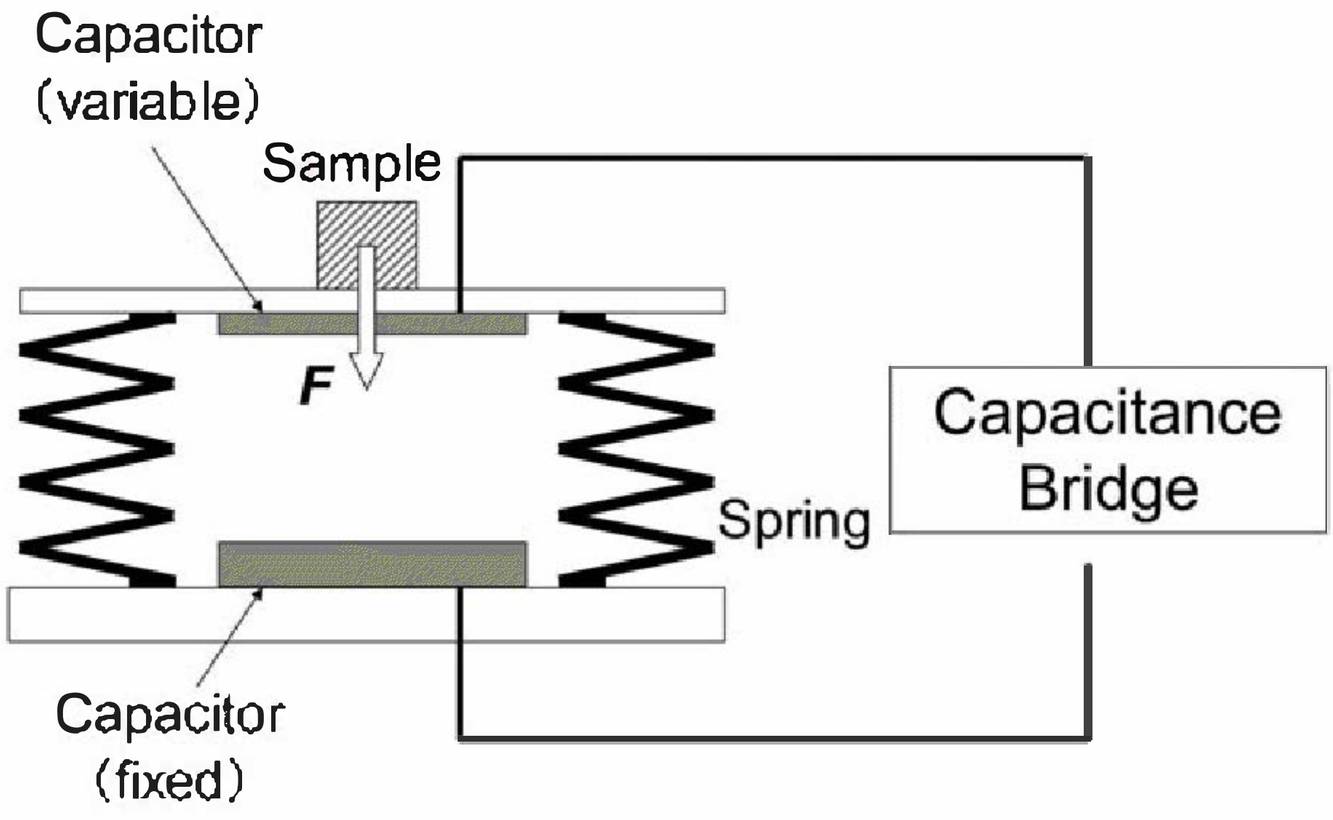


**Figure 1.4** Principle of the capacitance method.[5]

Moreover, due to its high natural frequency, it is also applicable under pulsed high magnetic fields. As shown in Figure 1.3, the torque $\boldsymbol{N}$ acting between the magnetic field $\boldsymbol{H}$ and the magnetic moment $\boldsymbol{m}$ of the sample on the cantilever causes deflection of the cantilever, which is detected as a change in electrical resistance.[4] There is also a method to measure magnetic force through changes in the capacitance of a parallel plate capacitor (capacitance method), as shown in Figure 1.4. This method is used for static magnetic measurements in cryogenic regions because there is no friction due to sample movement and no heat generation due to induced currents.[5]

### 1.2.2 Electromagnetic Induction Method

The electromagnetic induction method measures the induced electromotive force in the form of an induced voltage generated in the direction that interferes with the change in the magnetic flux penetrating the pick-up coil.

When the magnitude of the magnetization $M$ of the sample in a uniform magnetic field or the relative position of the sample to the pick-up coil changes with time, the pick-up coil generates an induced electromotive force $V$ proportional to the time derivative of the magnetic flux $\Phi$ that penetrates the pick-up coil (eqn (1.8)).

$$V = -\frac{d\Phi}{dt} \tag{1.8}$$

From the relation $\Phi = kM$ ($k$ is the proportional constant), $M$ is obtained as the integral value of eqn (1.8) concerning time, where $k$ depends on the sample shape, coil shape, *etc.*

$$M = \frac{1}{k}\int_0^t V dt \tag{1.9}$$

There are four representative methods for generating induced electromotive force.

(1) Vibrate the sample between the pick-up coils (**vibrating sample magnetometer (VSM) method**, Figure 1.5(a)).
(2) Vibrate the pick-up coils around the sample (**vibrating coil magnetometer (VCM) method**, Figure 1.5(b)).
(3) Move the sample in a certain direction in the pick-up coil (**extraction method**).
(4) Vary the magnetic field (**pulse magnetic field measurement, AC magnetic susceptibility measurement**).

For (1) and (2), the induced electromotive force $V$ shows a periodic variation concerning time, while for (3), it does not. For (4), when a pulsed magnetic field is used, $V$ shows a non-periodic time variation, and $M$ can be

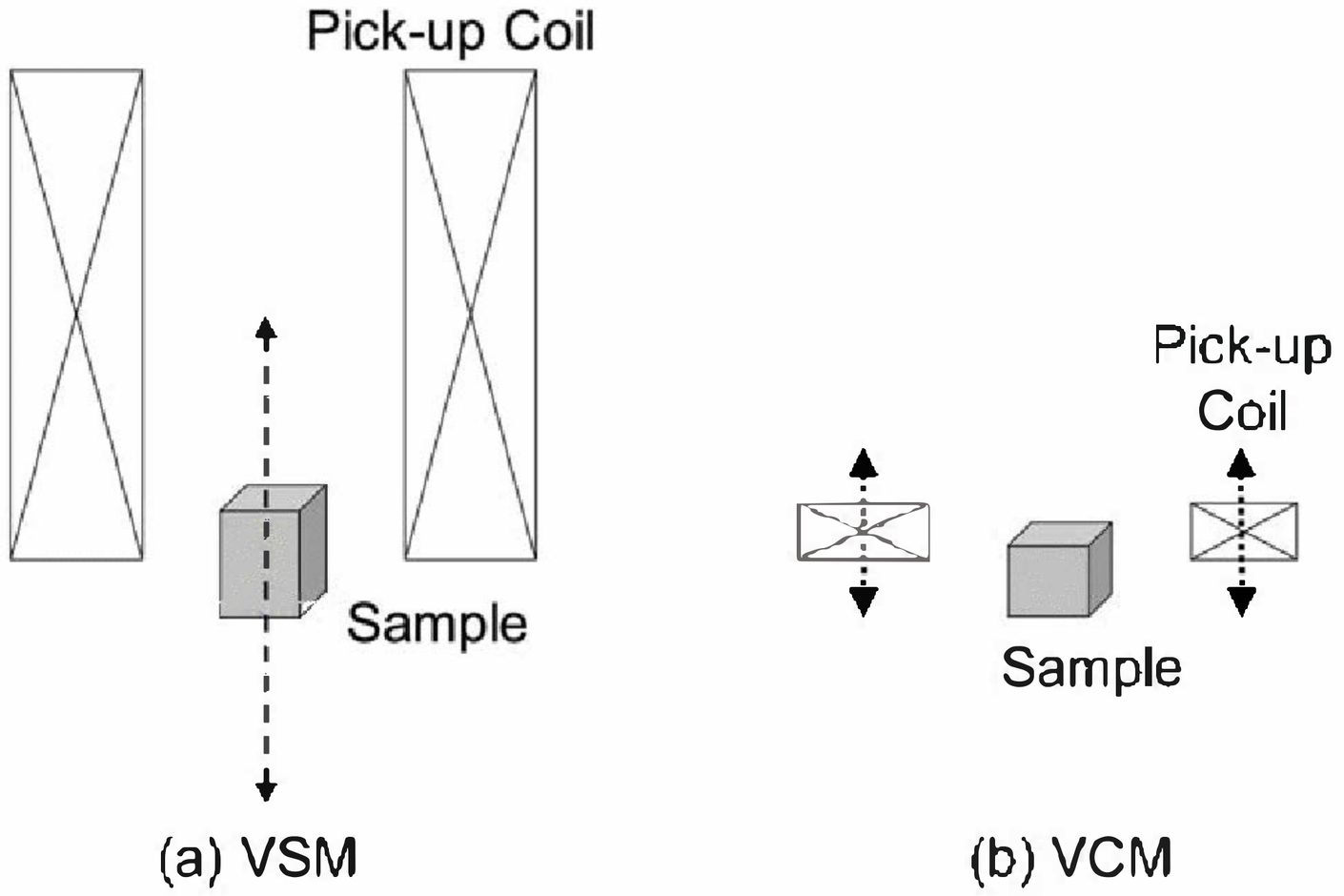


**Figure 1.5** (a) VSM method and (b) VCM method.

calculated by integrating $V$ over time (eqn (1.9)). In the case of (4) using AC magnetic field, $V$ will show a periodic time variation and give an AC magnetic susceptibility, which is out of the category of DC measurement. Methods (1)–(3) are outlined below.

(1) **The vibrating sample magnetometer (VSM)** uses a coil to detect changes in magnetic flux when a magnetized sample is vibrated at a constant frequency, where the generated induced electromotive force $V$ is proportional to the magnetization value $M$ of the sample. The vibration amplitude is calculated by lock-in detection, which has the advantage that the signal can be separated from noise components such as power supply noise. The pick-up coils may be located away from the sample but are often placed in the vicinity of the sample. Since the VSM method is a relative measurement, it must be calibrated using a standard sample with a known magnetization value to evaluate the absolute value in the measurement. With this in mind, the VSM is the most versatile magnetization measurement device using the electromagnetic induction method at the laboratory level.

(2) **The vibrating coil magnetometer (VCM)** is an apparatus in which the sample position is fixed, and the pick-up coil is vibrated. When a thin pick-up coil is used, it is vibrated near the position where the magnetic flux from the sample changes with the largest position derivative.[6] So, it is not always good to place the pick-up coils at the same height as the sample. VCM is effective when the sample and pick-up coils must be spatially separated, but it is less popular than VSM.

(3) **The extraction method** has long been used in many high magnetic field facilities to measure magnetization curves under high magnetic fields. The advantage is that measurements can be performed efficiently even with slow sweep-speed magnets, such as high-field superconducting magnets. However, since the sample is moved significantly between the coils, magnetization and demagnetization are repeated at each sample movement. This has the disadvantage that the measured value fluctuates per measurement for samples exhibiting magnetic hysteresis, such as in ferromagnetic materials. Figure 1.6 shows an example of the extraction method using a superconducting magnet. This system is designed to measure under multiple extreme environments of high magnetic field, high pressure, and low temperature.[7] Figure 1.7 shows the change in induced voltage $V_1$ when the sample is extracted from the pick-up coils. Point A is the starting point of the movement, and the voltage at point A is the offset voltage $V_0$. Between points B and C, the sample moves inside the space between the pick-up coils. The area of the shaded part is determined from the maximum and minimum values of the induced current $I$. It is proportional to the $M$ of the sample, independent of the sample extracting speed.

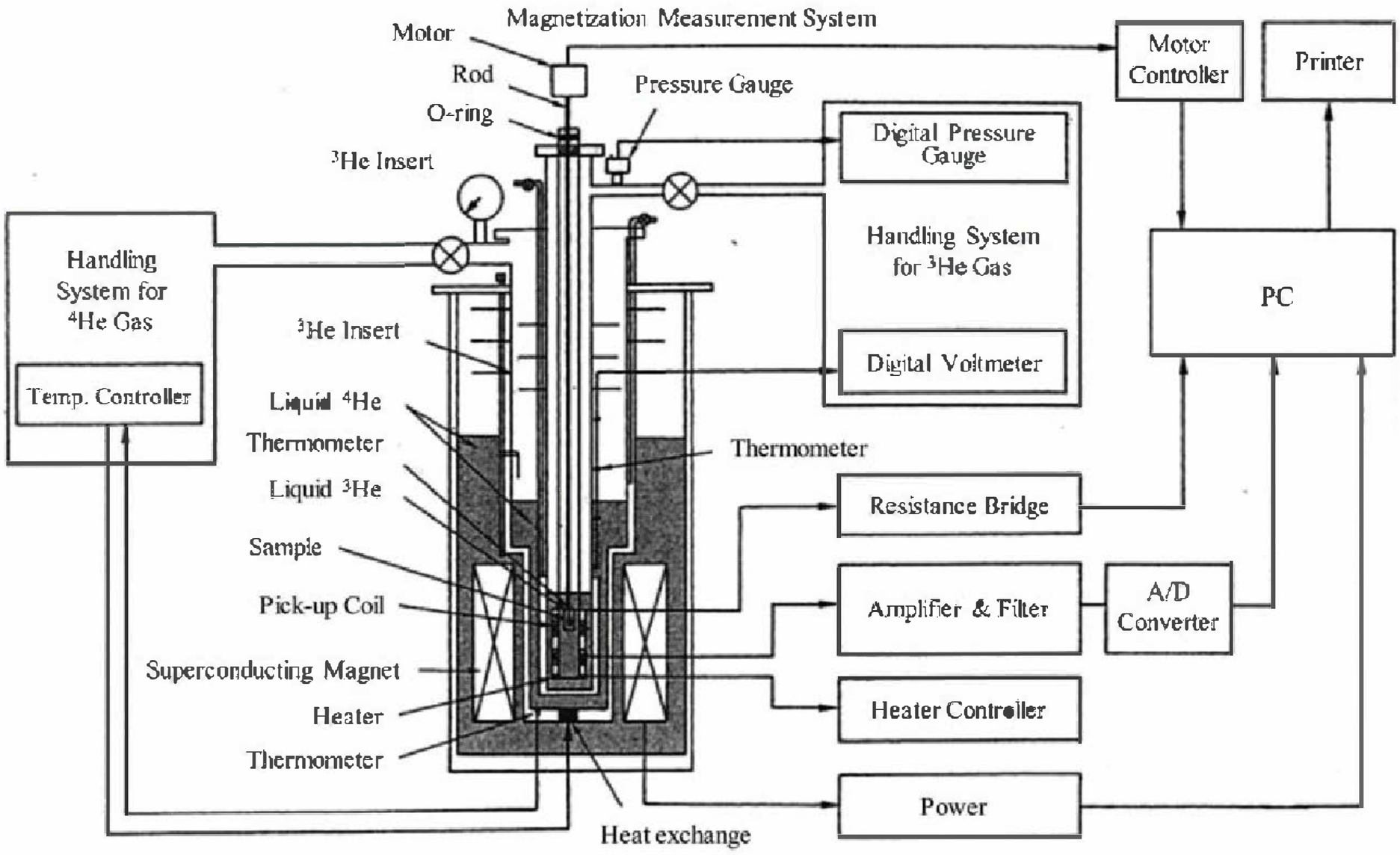


**Figure 1.6** Block diagram of the magnetization measurement system using the extraction method under multiple extreme conditions of the high magnetic field, high pressure, and low temperature.[7] Adapted from ref. 7 with permission from AIP Publishing, Copyright 1998.

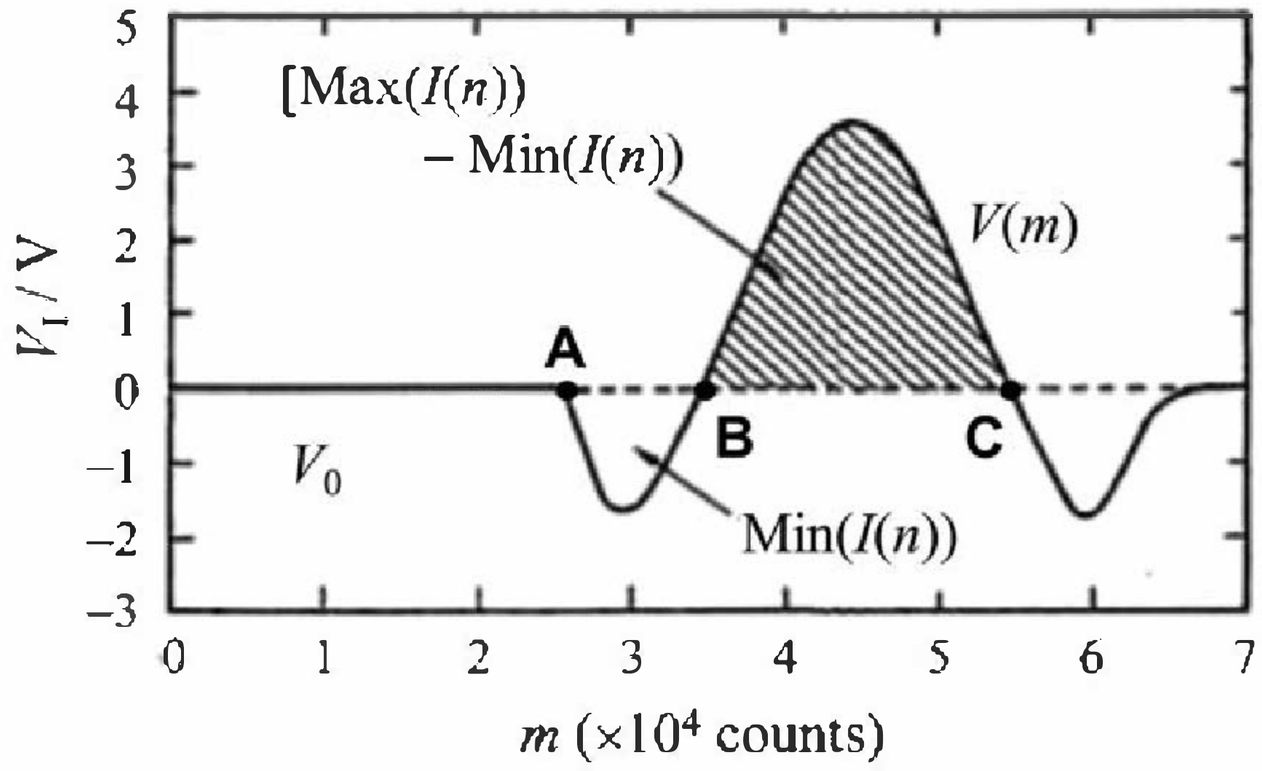


**Figure 1.7** Variation of the signal voltage generated in the magnetization pick-up coils by the extraction method. The area of the shaded part is proportional to $M$ of the sample.[7] Adapted from ref. 7 with permission from AIP Publishing, Copyright 1998.

### 1.2.3 SQUID Method

A SQUID is a weakly coupled superconducting device (Josephson junction) that can directly measure changes in the magnetic flux $\Phi$. The tunnel current flowing between junctions is modulated by the number of magnetic fluxes, and the voltage across SQUID has periodic characteristics concerning changes in magnetic flux. A SQUID magnetometer measures the number of magnetic fluxes produced by a sample as quantum flux $\Phi_0$ ($= 2.06783461 \times 10^{-15}$ Wb)

units using the above principle. The basic structure of a SQUID magnetometer consists of a SQUID for magnetic flux detection, a magnetic flux conversion circuit that transmits the magnetic flux of the measurement space to the magnetic flux detection section, and an electronic circuit to extract voltage signals from the SQUID. Typically, a feedback mode is used to linearize the nonlinear characteristics between the voltages across the SQUID and the magnetic flux changes. Such a flux-locked loop (FLL) circuit, commonly called the zero detection method, can provide a detection sensitivity that is about 1/100 for $\Phi_0$. The measurement sensitivity is superior to other general-purpose measurement methods.

There are two types of SQUIDs: rf-SQUIDs, which have one Josephson junction in the superconducting ring, and dc-SQUIDs, which have two.[8,9] Figure 1.8 shows a block diagram of the rf-SQUID system.[8] Firstly, the tank circuit (LC parallel resonance circuit) is excited by a constant current source at its resonant frequency (typically in the rf band of 20–30 MHz). The rf-SQUID is driven by circulating current in the ring due to electromagnetic induction. The voltage of the tank circuit coupled to the rf-SQUID is amplified and detected, followed by phase detection at the modulation frequency. The output is fed back to the SQUID by a resistor $R_{FB}$ and feedback coil. Figure 1.9 shows an example block diagram of a dc-SQUID system driven by a DC current source. While rf-SQUIDs resist external disturbances (noise), they are inferior to dc-SQUIDs in terms of sensitivity. On the other hand, dc-SQUIDs have the advantages of high sensitivity and fast response but are more susceptible to external disturbances than rf-SQUIDs.

The advantage of SQUIDs is that they can provide high reliability as well as high measurement accuracy when fabricating general-purpose devices. However, there is a problem that the pick-up coil, which consists of a superconducting wire (typically NbTi with a superconducting transition temperature of 9 K), must be maintained below the superconducting transition temperature during the measurement. To perform measurements over

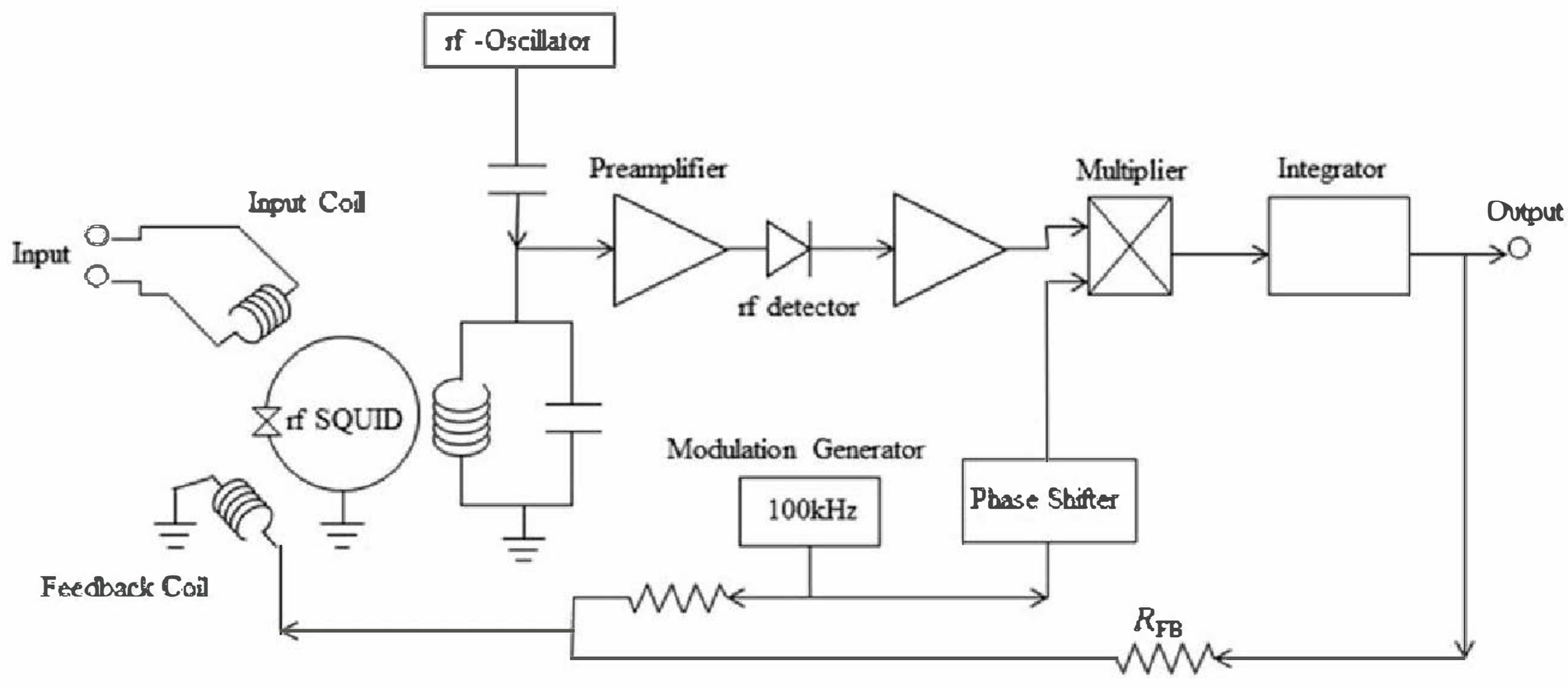


**Figure 1.8** A block diagram of the rf-SQUID system.[8]

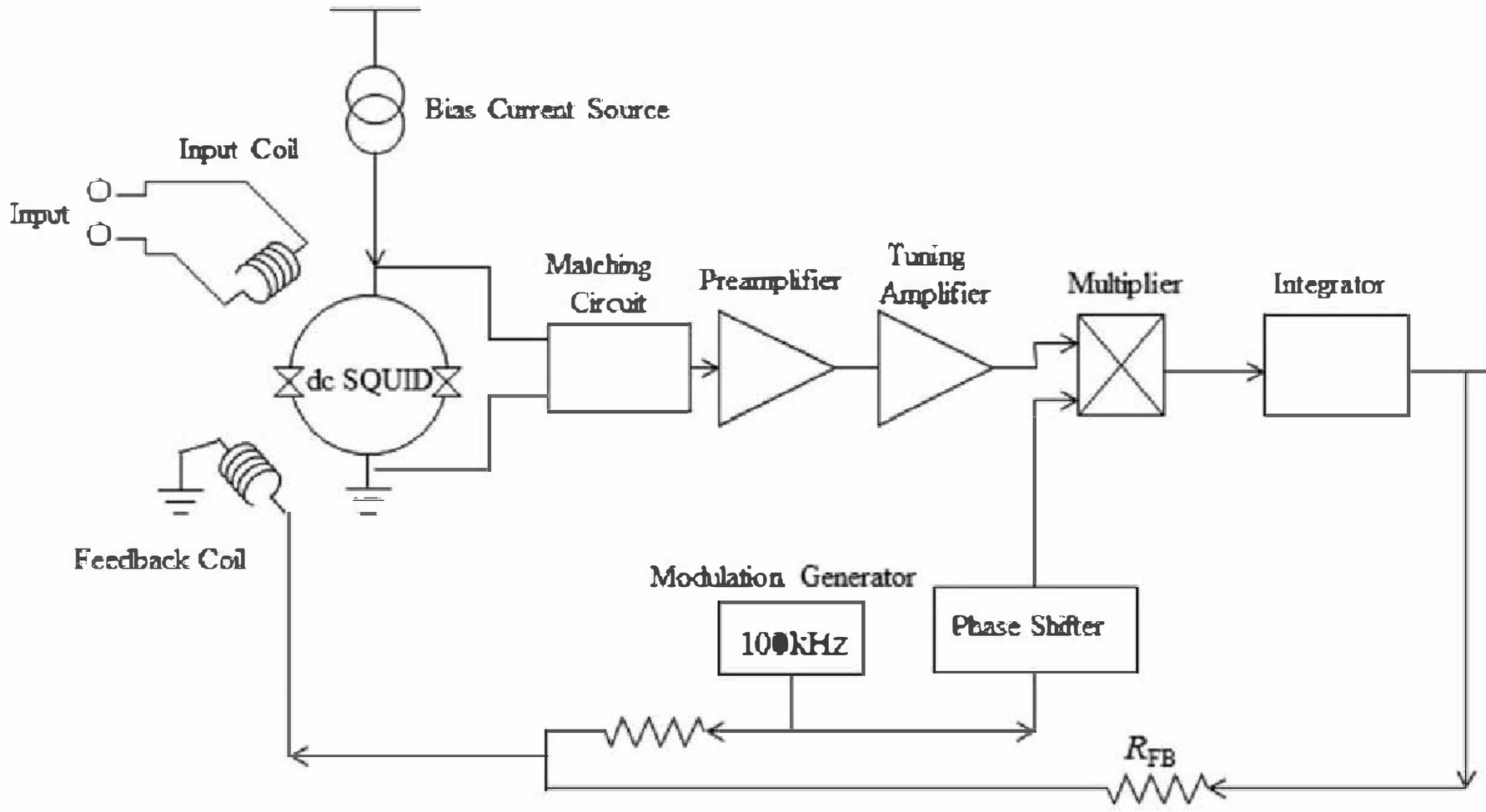


**Figure 1.9** A block diagram of the dc-SQUID system.[8]

a wide temperature range, the pick-up coil must be thermally isolated from the sample space and placed in a low-temperature heat bath, even at the expense of detection sensitivity. If the pick-up coil is placed close to the sample to increase its filling factor, the temperature of the pick-up coil may increase with increasing the sample temperature, which will cause the SQUID system to fail.

### 1.2.4 Difference Between the SQUID and Electromagnetic Induction Methods – Superconducting and Normal-conducting Magnetic Flux Conversion Method

The SQUID method includes the micro-SQUID method, in which the SQUID itself is used as the pick-up coil, but this is not suitable for conventional SQUID magnetometers in which the sample is frequently replaced. Therefore, we place the sample at a distance from the SQUID and use a mechanism to transmit the change in magnetic flux to the SQUID. Usually, a magnetic flux conversion circuit is employed for this mechanism, in which a closed loop is formed with the pick-up coil that detects the magnetic flux of the sample, and the signal coil that transforms the magnetic flux signal to the SQUID (Figure 1.10). Here, the self-inductance of the SQUID is described as $L$, and the self-inductance and the winding number of both the pick-up coil and the signal coil are described $L_1$, $n_1$, and $L_2$, $n_2$, respectively. The optimization of this magnetic flux conversion circuit is so important that it affects the accuracy of magnetic measurements. Consider the following two cases; case 1, that all of the magnetic flux conversion circuits are in the superconducting state, and case 2, that some or all are in the normal conducting state. Case 2 corresponds to the abovementioned case of which the pick-up coil made of superconducting wire is placed close to the sample and

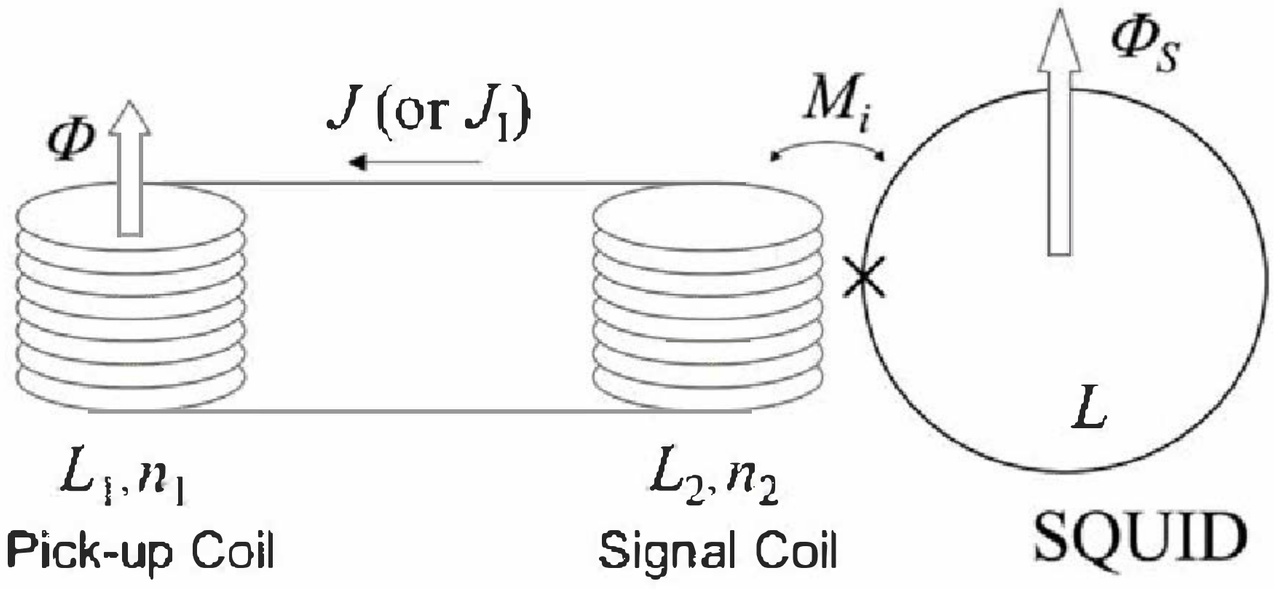


**Figure 1.10** Magnetic flux conversion circuit.

changed to the normal-conductive state due to the sample temperature increase.

When the magnetic flux conversion circuit is all in a superconducting state and a superconducting closed loop is realized, it is called a superconducting magnetic flux conversion scheme. In this circuit, the magnetic flux $\Phi$ penetrating the circuit is kept constant. If the pick-up coil senses a magnetic flux change in $\Phi$, the superconducting current $I$ flows through the circuit, which counteracts the change, satisfying eqn (1.10).

$$\Phi n_1 + (L_1 + L_2)I = 0 \tag{1.10}$$

In this case, a magnetic flux change $\Phi' = L_2 I$ is induced in the signal coil, which is equal in magnitude but opposite in sign to that of the magnetic flux change in $\Phi$. The magnetic flux change $\Phi$ in the signal coil provides magnetic flux $\Phi_S$ to the SQUID through mutual inductance $M_i$.

$$\Phi_S = M_i I \tag{1.11}$$

The advantage of this detection method is that it can transmit a direct current (steady) signal using a superconducting current always flowing in the circuit, *i.e.*, directly detecting static magnetization. Here, the relationship, eqn (1.12), is held between the magnetic flux change in $\Phi$ detected in the pick-up coil and the magnetic flux $\Phi_S$ transmitted to the SQUID.

$$\Phi_S = -\frac{M_i n_1}{L_1 + L_2}\Phi \tag{1.12}$$

The coils should be designed to maximize $\Phi_S$ so that $M_i n_1/(L_1 + L_2)$ is maximized. Maximizing $M_i n_1/(L_1 + L_2)$ and increasing $M_i$ makes the coupling constant $K$ ($K^2 = M_i^2/L_1 L_2$) close to 1, finally leading to the condition of $L_1 = L_2$.

Next, consider the case where the superconducting loop of the magnetic flux conversion circuit is fallen to normal-conductive. This is the normal-conducting magnetic flux conversion scheme instead of the superconducting one described above. When a time-varying magnetic flux $\Phi$ is given to the pick-up coil, an induced electromotive force $V$ is generated in the circuit and an induced current $I_I$ flows accordingly. $V$ and $I_I$ through the circuit are given by eqn (1.13) and (1.14), respectively, where $Z_1$ $(= i\omega L_1)$ and $Z_2$ are the