Nuclear Magnetic Resonance and Its Application in Condensed Matter Physics

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1. Introduction

Nuclear Magnetic Resonance (NMR) is a physics phenomenon first observed by Isidor Rabi in 1938. [1] Since then, the NMR spectroscopy has been applied in a wide range of areas such as physics, chemistry, and medical examination. In this paper, I want to briefly discuss about the theory of NMR spectroscopy and its recent application in condensed matter physics.

2. Principles of NMR

NMR occurs when some certain nuclei are in a static magnetic field and another oscillation magnetic field. Assuming a nucleus has a spin angular momentum $\vec{I} = \hbar m_I$, then its magnetic moment $\vec{\mu}$ is

$$\vec{\mu} = \gamma \vec{I} \tag{1}$$

The γ here is the gyromagnetic ratio, which depends on the property of the nucleus. If we put such a nucleus in a static magnetic field $\vec{B}_0$, then the magnetic moment of this nuclei will process about this magnetic field. Therefore we have, [2] [3]

$$\vec{\tau} = \vec{\mu} \times \vec{B}_0 = \frac{d\vec{I}}{dx} = \frac{1}{\gamma}\frac{d\vec{\mu}}{dx} \tag{2}$$

From this semiclassical picture, we can easily derive that the precession frequency ω_0 (which is called the Larmor angular frequency) is

$$\omega_0 = \gamma B_0 \tag{3}$$

Then, if another small oscillating magnetic field is added to the plane perpendicular to $\vec{B}_0$, then the total magnetic field is (Assuming $\vec{B}_0$ is in $\hat{z}$ direction)

$$\vec{B} = B_0\hat{z} + B_1(\cos(\omega t)\,\hat{x} + \sin(\omega t)\,\hat{y}) \tag{4}$$

If we choose a frame $(\hat{x}', \hat{y}', \hat{z}' = \hat{z})$ rotating with the oscillating magnetic field, then the effective magnetic field in this frame is

$$\hat{B}_{eff} = \left(B_0 - \frac{\omega}{\gamma}\right)\hat{z} + B_1\hat{x}' \tag{5}$$

As a result, at $\omega = \gamma B_0$, which is the resonant frequency, the $\hat{z}$ component will vanish, and thus the spin angular momentum will precess about $\vec{B}_1$ instead. Furthermore, if the time t that the oscillating field is applied and the Larmor frequency $\omega_0 = \gamma B_1$ satisfies

$$\omega_0 t = \pi/2 \tag{6}$$

The spin will rotate 90° and therefore into the xy-plane. Such a pulse is call a 90° pulse. Similarly, a pulse that will rotate the spin by 180° is call a 180° pulse which is twice as long as a 90° pulse.

However, because in general the sample consists of many atoms, the NMR signal measured is the combination effect of all these atoms. Each atom has two states in a given magnetic field $\vec{B}_1$, which are

$$E = \pm\mu B_0 \tag{7}$$

So, the energy difference is

$$\Delta E = 2\mu B_0 \tag{8}$$

Therefore, the ratio of the amount of atoms in two difference states obeys the Boltzmann distribution,

$$\frac{N_+}{N_-} = \frac{e^{\mu B_0/kT}}{e^{-\mu B_0/kT}} = e^{\Delta E \cdot B_0/kT} \tag{9}$$

The net magnetization of the sample along z axis is

$$M_0 = \mu(N_+ - N_-) = N\mu\tanh(\frac{\mu B_0}{kT}) \tag{10}$$

Consequently, after a 90° pulse, the net magnetization will be rotated to xy-plane. Afterwards, the net magnetization will decay exponentially due to the thermal relaxation, which

is known as spin-lattice relaxation, and dissipate energy to the lattice. In the end, the net magnetization will recover back to $\hat{z}$ direction. During the spin-lattice relaxation, the net magnetization in $\hat{z}$ direction is

$$M_z(t) = M_0(1 - e^{-\frac{t}{T_1}}) \tag{11}$$

T_1 in the equation (11) is called the spin-lattice relaxation time.

Besides spin-lattice relaxation, the net magnetization will also start to dephase after the 90° pulse. The reason is that each spin is in slightly different environment and its precession frequency thus differs from γB_0 by different amounts because of the magnetic dipole interactions [2], even though the difference is small. As a result, the net magnetization in xy-plane after the 90° pulse will decay exponentially, which is known as spin-spin relaxation.

$$M_{x,y}(t) = M_0 e^{-\frac{t}{T_2}} \tag{12}$$

T_2 in equation (12) is called the spin-spin relaxation time.

3. Experimental Method Used in NMR Spectroscopy

In the experiments, there are usually two ways to get the NMR spectroscopy, the free induction decay and the spin echo measurement.

The free induction decay is a really simple method. After simply sending a 90° pulse to the sample, the responding signal from the sample is measure along $\hat{x}$ direction. Therefore, the signal measured will be the combining effect of the spin-lattice relaxation and the precession about the static field $\vec{B}_0$. A sample signal in time

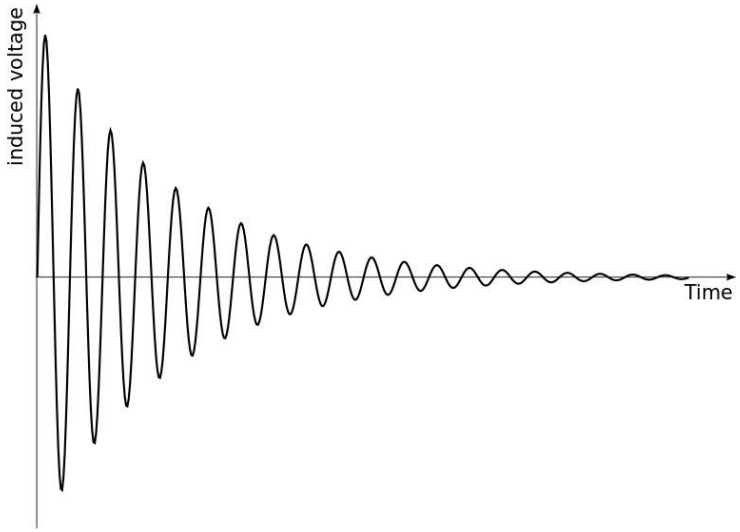

Figure 1. Free Induction Decay (FID) nuclear magnetic resonance signal seen from a well shimmed sample

domain is shown in figure 1[1]. By doing the Fourier transform on the signal in time domain, we can get the NMR spectroscopy in frequency domain and therefore find the resonance frequency of the specific nucleus that we measured. Moreover, from the signal in time domain, we can observe the decay of the peak, which is caused by spin-lattice relaxation, from this decay we can also figure out the T_1 for the certain nucleus.

The spin echo measurement is more complicated than the free induction decay. In spin echo measurement, a 90° pulse is first applied on the sample, which will rotate the net magnetization to the $\hat{x}$ axis as discussed before. Then the spins start to dephase and rotates in xy-plane at different rate. After a short period of time τ, a 180° pulse is applied and therefore flips the spin in xy-plane. After the 180° pulse, because all the spins are flipped and they have to rotate in the same direction all the time, the spin will start to gather again and eventually come together in -$\hat{x}$ direction after the amount of time τ. If the signal is measured from this time, then we can get a similar signal in time domain as in figure 1. This whole process is illustrated in figure 2[2] [4] (However, the time label is different from the discussion here).

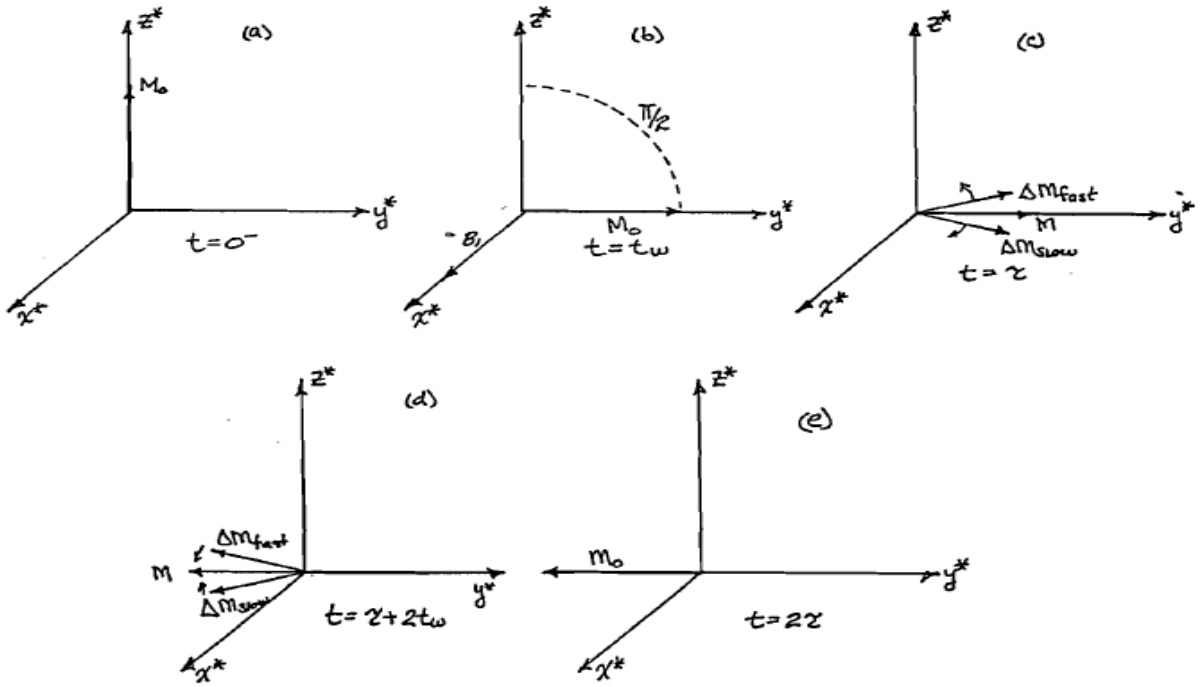

Figure 2. The magnetization a.) Before any pulses b.) After the 90° pulse c.) The pulse begins to decay d.) After the 180° pulse e.) When the pulse reforms

[1] http://en.wikipedia.org/wiki/Free_induction_decay
[2] TeachSpin Instructional Pulsed NMR Apparatus Instruction Manual

In the practical use, both methods have their own advantages. In the experiment setup, a LC circuit (used for amplifying the pulse intensity) consisting of a coil and a proper inductor is usually used to add the oscillating magnetic field on the sample. Therefore, for the free induction decay, after the 90° pulse, it will take a short period of time to let the pulse in the coil decay and vanish completely before we can measure the signal, since the pulse is in general much bigger than the NMR signal from the sample. However, if T_1 in the sample is much smaller than this required time, then the measured signal will be really low because of that. In spin echo measurement, however, because there is a time interval τ between the 180° pulse and the start of the measurement, usually the decay of 180° pulse will not interfere with the signal. The time τ can be chosen as any value as long as most of the spin has not gone back to the equilibrium position. Nevertheless, spin echo measurement also has its drawbacks. For example, there are more parameters to adjust in spin echo measurement, the length of 90° and 180° pulse, τ, etc. Therefore, sometimes it will be hard to get a good signal with spin echo measurement.

4. Applications of NMR in Condensed Matter Physics

In general, NMR technique is suitable for any nuclei that have non zero spin, such as ^{1}H, ^{2}H, ^{13}C, ^{27}Al, etc. Among all of them, ^{1}H and ^{13}C are two of the widely used atoms. In recent years, the NMR spectroscopy of ^{13}C has been used a lot in the study of organic superconductors. Because the NMR spectra as well as the spin-lattice relaxation time T_1 are dependent on the nearby environment of the nuclei, the NMR study can therefore be a powerful tool to study the phase transition and other features in superconductors from the related shift in NMR spectra's peak and the change of relaxation time.

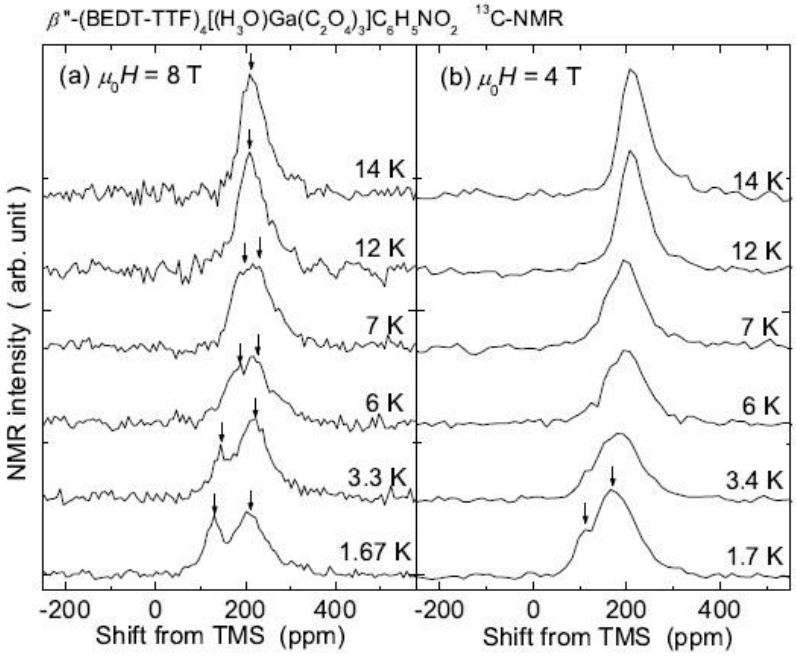

Figure 3. 13C NMR spectra of β ''-(BEDT-TFF)4[(H3O)Ga(C2O4)3]•C6H5NO2 at magnetic fields of 8 T and 4 T

Last year, professors at Hokkaido University in Japan

did the ^{13}C NMR study in one of the organic superconductors, β′′-(BEDT-TFF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]•C$_6$H$_5$NO$_2$ in order to study the superconductivity near charge instability. By measuring the ^{13}C NMR spectra, they have observed that the single peak was found at 14 K, but it broaden and split into two peaks as the temperature lowers (Figure 3). [5] However, there are still a few possible explanation for this observation. In order to find the right reason for the peak split, some other experiments were done, such as the measurement of the NMR shift, the full widths at half maximum (FWHM), and T_1 (Figure 4 and 5). From the FWHM measurement, the abrupt increase of the measurement was observed near 12 K and can be therefore determined as the onset temperature of the NMR spectra splitting. Moreover, the measurement on the resistivity also shows that the electrical properties are changed near 12 K. Since the FWHM measurement shows that the line width of the NMR spectra does not change with the external field, it can be therefore concluded that the splitting is not caused by the magnetic transition, which predicts a dependence in the external field. Also, in the measurement of the resistivity, the transition temperature for superconductivity T_C can be determined, which is much lower than the onset temperature 12 K under different magnetic fields. As a result, a

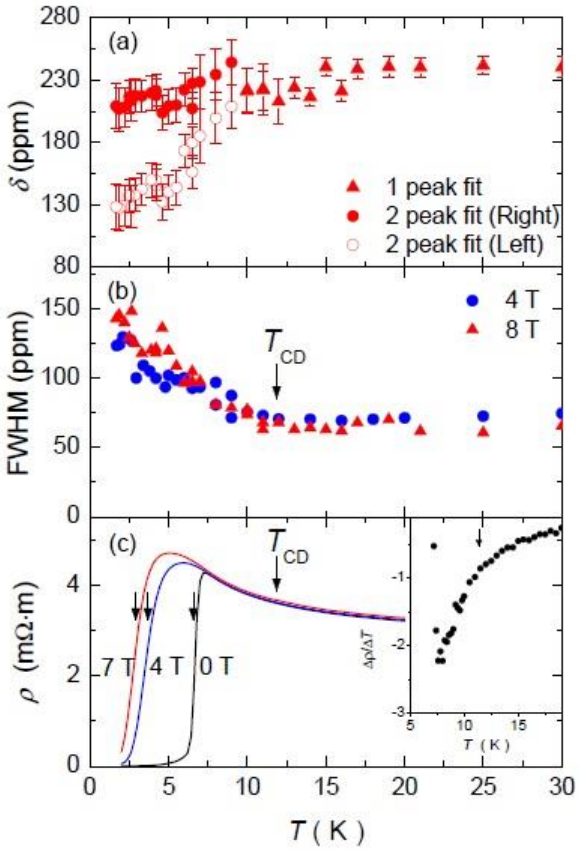

Figure 4. (a) Temperature dependence of NMR shift in 8T. (b) FWHM measurement at 4 T and 8 T. (c) In –plane resistivity measurement

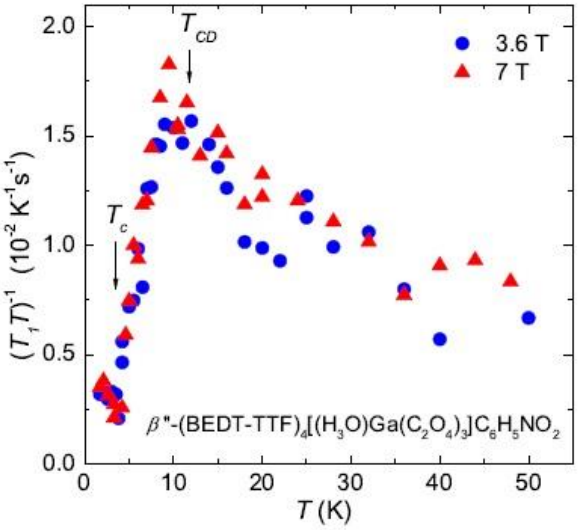

Figure 5. Temperature dependence at 3.6 T and 7 T

transition to superconducting phase can be also excluded as the reason for the splitting in NMR spectra. After excluding all other possible reasons, the experimental results in NMR study suggest that the splitting is ascribed to the charge instability, and therefore in β′′-(BEDT-TFF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$]•C$_6$H$_5$NO$_2$, a charge-disproportionate state is achieved at low temperature.

5. Summary

NMR is a phenomenon that has been discovered for a long time. Throughout the time, the basic experimental methods for NMR measurements are free induction decay and spin echo measurement, both of which have their own advantages. In recent years, NMR study is still widely used in condensed matter physics. One of the most recent results is the ^{13}C NMR measurement in a specific kind of superconductor, β′′-(BEDT-TFF)$_4$[(H$_3$O)Ga(C$_2$O$_4$)$_3$] •C$_6$H$_5$NO$_2$. From the NMR study, the authors conclude that this material undergoes a change to a charge-disproportionate state at low temperature, and also propose a relationship between the charge instability and superconductivity.

Reference

1. Rabi, I.I.; Zacharias, J.R.; Millman, S. and Kusch, P. (1938). "A New Method of Measuring Nuclear Magnetic Moment". *Physical Review* 53 (4): 318–327.

2. Slichter, C. P., Principles of magnetic resonance, 2nd Ed., Springer-Verlag, Berlin, 1978.

3. University of Illinois, Pulsed Nuclear Magnetic Resonance. Lab Manual.

4. TeachSpin Instructional Pulsed NMR Apparatus Instruction Manual

5. Ihara, Yoshihiko, Harumi Seki, and Atsushi Kawamoto. "13C NMR Study of Superconductivity near Charge Instability Realized in β"-(BEDT-TTF) 4 [(H3O) Ga (C2O4) 3]· C6H5NO2." *Journal of the Physical Society of Japan* 82.8 (2013).