Nonlinear Magnetic Susceptibility Measurements at GPa-Level Pressures

M Mito 1, S Tominaga 1, Y Komorida 1, H Deguchi 1, S Takagi 1, Y Nakao 2, Y Kousaka 2 and J Akimitsu 2
1Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan
2Department of Physics and Mathematics, Aoyama Gakuin University, Sagamihara 229-8558, Japan
E-mail: mitoh@tobata.isc.kyutech.ac.jp

Abstract. The second nonlinear susceptibility, $\chi^{(2)}$, reflects magnetic domain formation. At zero DC field, the temperature dependence of $\chi^{(2)}$ can be obtained through that of the third-harmonic AC susceptibility, $\chi_{3\omega}$. Generally, the magnitude of $\chi_{3\omega}$ is at most a few percent of the linear component, $\chi_{1\omega}$, connected with the linear susceptibility, $\chi^{(0)}$. At GPa-level pressures generated using a diamond anvil cell, the detection of $\chi_{3\omega}$ becomes more difficult, because of the small amount of measurement sample. We propose an effective method of measuring $\chi_{3\omega}$ using a superconducting quantum interference device magnetometer and a statistics average technique. The experimental results for an inorganic chiral magnet, Cr$_{1/3}$NbS$_2$, indicate the efficiency of this technique and demonstrate that magnetic signals of the order of $10^{-9}$ emu can be detected.

1. Introduction
Magnetic measurement at GPa-level pressures ($P$) often faces the problem of measurement sensitivity, because of the insufficient amount of measurement sample. Nowadays, the combination of a piston cylinder-type of pressure cell and a commercial superconducting quantum interference device (SQUID) magnetometer, MPMS (Quantum Design), is popular for magnetic measurement at pressures up to approximately 1 GPa. For $P > 1$ GPa, a diamond anvil cell (DAC) or a cubic anvil cell is often used, whose combination with SQUID has not been popular among materials scientists. Furthermore, measurement of minute nonlinear magnetic susceptibility at GPa-level pressures has been extremely rare.

Ishizuka et al. have successfully performed magnetic susceptibility measurement at pressures of up to 160 GPa by the vibrating coil magnetometer method using SQUID [1]. A high accuracy of $10^{-10}$ to $10^{-11}$ emu has been achieved by placing the detection coil near the sample in DAC and compensating the magnetic-field signal [2]. The observed quantity is the magnetic flux in a certain DC magnetic field, yielding the DC susceptibility. The upper limit of temperature range is about the liquid-nitrogen temperature, as a problem of the setup. Mito et al. have presented another style of magnetic measurement: the use of a miniature DAC and the commercial SQUID magnetometer for GPa-level pressures [3-8]. In this method, the sample is placed far from the liquid-helium thermal bath, in which a detection coil with a diameter of 20 mm, an AC exciting coil and a superconducting magnet for the
DC field are located. This method has some benefits, such as (1) the coverage of a wide temperature region, from 1.8 K to 400 K, (2) the possibility of applying both an AC field and a DC field, and (3) the possibility of observing both the AC susceptibility at 0.1 Hz–1 kHz and the magnetization. In the ordinal measurement method, the sensitivity is on the order of $10^{-7}$ emu. In this report, we attest to the validity of the statistic average technique for the improvement of the sensitivity up to the $10^{-9}$ level, and verify the performance through the nonlinear magnetic susceptibility measurements in an inorganic chiral magnet, Cr$_{1/3}$NbS$_2$.

Generally, the magnetization, $M$, can be expanded by the magnetic field, $H$, as follows:

$$M = \chi^{(0)} H + \chi^{(1)} H^2 + \chi^{(2)} H^3 + \chi^{(3)} H^4 + \chi^{(4)} H^5 + \cdots$$  \hspace{1cm} (1)

where $\chi^{(0)}$ is the linear susceptibility, and $\chi^{(m)} (m \neq 0)$ is the nonlinear susceptibility. Under an AC field of $H_{AC} = h \cos \omega t$, $M$ can be expanded as follows:

$$M(t) = M_{m0} \cos \omega t + M_{2m0} \cos 2\omega t + M_{3m0} \cos 3\omega t + M_{4m0} \cos 4\omega t + \cdots$$  \hspace{1cm} (2)

where $\omega$ is the angular frequency, and $M_{n0} = h \chi_{n0} (n = 1, 2, 3, \cdots)$ stands for the $n$th-harmonic component. Herein, the out-of-phase components are neglected for the sake of simplicity of the explanation. At zero residual DC field, the power expansion with the cosine function after replacing $H$ in equation (1) with $h \cos \omega t$ yields:

$$\chi_{10} = \chi^{(0)} + \frac{3}{4} \chi^{(2)} h^2 + \frac{5}{8} \chi^{(4)} h^4 + \cdots, \chi_{20} = \frac{1}{2} \chi^{(3)} h + \frac{3}{2} \chi^{(5)} h^3 + \cdots, \chi_{30} = \frac{1}{4} \chi^{(4)} h^2 + \frac{5}{16} \chi^{(6)} h^4 + \cdots$$  \hspace{1cm} (3)

The large signal of $\chi^{(1)}$ reflects the existence of spontaneous magnetization, and the anomaly of $\chi^{(2)}$ reflects magnetic domain formation [9-11]. The long-range magnetic domain is the long-range scale of the magnetic domain. At small $h$ values, $\chi_{10}$ mainly reflects $\chi^{(0)}$, while $\chi_{20}$ and $\chi_{30}$ are connected with $\chi^{(1)}$ and $\chi^{(2)}$, respectively [12]. At zero DC field after zero-field cooling, $\chi_{20}$ becomes quite small. Generally, the magnitude of $\chi_{30}$ is at most a few percent of $\chi_{10}$, and its detection is quite difficult in high-pressure experiments using DAC. Here, we propose an effective method of measuring $\chi_{30}$ at high pressures by means of the SQUID magnetometer and a statistics average of the analytic values resulting from fast Fourier transformation (FFT).

2. Experimental

Cr$_{1/3}$NbS$_2$ is an easy-plane ferromagnet with a Curie temperature ($T_C$) of 127 K, and the ferromagnetic moment on the $c$-plane modulates along the $c$-axis with a periodicity of 480 Å [13]. This material belongs to the space group $P6_322$, and the lattice constants are $a = 5.75$ Å and $c = 12.12$ Å. In the present experiment, single crystals with a size of 0.1 mm × 0.05 mm × 0.1 mm were used.

Pressure was created by means of a miniature DAC, which could be inserted into MPMS [3]. The cuvet diameter size of the diamond anvils was 1.0 mm. A CuBe gasket with a thickness of 0.2 mm was used, and the diameter of the sample chamber was 0.5 mm. A few single crystals were arranged in the sample chamber, keeping the $c$-plane parallel with the vertical direction. In the void space, Apiezon-J oil as a pressure transmitting medium was held with a few pieces of ruby. We know that daphne oil or fluorinated oil is better than the Apiezon-J oil for realizing hydrostatic condition. In this study, however, the Apiezon-J oil was used because of its good thermal conductivity and easy handling. The pressure value was estimated from the shift of the $R_1$ ruby fluorescence line at room temperature [14].

The AC susceptibility was measured by means of MPMS with the AC option. The amplitude of $H_{AC}$ was 4.0 Oe, and the frequency ($f = \omega/2\pi$) was 10 Hz. The same measurements were repeated under the same conditions 30 times. The digitalized wave patterns were gathered by the MultiVu software in MPMS, and the saved wave consisted of two cycles (= one block). At $f = 10$ Hz, there were 2,344 points (= $n$) per a block, and the sampling ratio, $f_s$, was 11.72 kHz. According to the sampling theorem, the frequency resolution, $\Delta f$, in FFT is determined by $\Delta f = f_s/n$, resulting in $\Delta f = 5$ Hz, which is equal to a half of $f$. In MPMS, both $f_s$ and $n$ vary with the frequency, so that $\Delta f = 0.5 f$ is always fixed.
Generally, $\chi_{3\omega}$ is likely to be buried in the $1/f$ noise and the line noise when using DAC, and this fixation of $\Delta f$ is not suitable for detecting minute signals.

3. Spectrum analyses for detecting small magnetic signals

**Approach 1: One FFT after taking the average of the wave pattern**

In order to improve the signal-to-noise (S/N) ratio of the wave pattern, 30 wave patterns were averaged, and FFT was performed only once for the averaged wave. At this time, $\Delta f$ remained $0.5f$.

**Approach 2: One FFT after setting the wave pattern in a row along the time axis**

Thirty wave patterns were set in a row along the time axis, and FFT was performed only once. The sampling number ($n$) consisting of a wave was increased to 30 times as much as that in each wave before being connected with each other. Consequently, $\Delta f$ became a $1/30$ of the initial value. This is desirable when distinguishing small amplitudes of $\chi_{3\omega}$ from the $1/f$ noise and the line noise.

**Approach 3 & 4: The mean (3) and median (4) of the analytic values resulting from thirty FFTs**

FFT for each wave block was repeated 30 times. Then, the mean (Approach 3) or median (Approach 4) of the 30 analytic values was calculated. $\Delta f$ remained $0.5f$. In the mean method, all of the thirty data had the same weight. The mean varies more sensitively to a few remarkable deviations of the analytic value from the optimum value. On the other hand, the median yields the value with the highest probability. When there is much distribution around the optimum value, the median converges upon the optimum more quickly. So as to obtain a reliable value for the median, at least 20 data are necessary.

4. Results

Figures 1 and 2 show the temperature dependences of the in-phase components of $\chi_{1\omega}$ and $\chi_{3\omega} (\chi_{1\omega}'$ and $\chi_{3\omega}')$, obtained by Approach 4, for Cr$_{1/3}$NbS$_2$ at $P = 0$ GPa and 3.1 GPa, respectively. The signal intensity of the observed $\chi_{3\omega}'$ was about $2\sim3 \times 10^{-9}$ emu, and the statistic average worked effectively for $\chi_{3\omega}'$. At a series of pressures, the anomaly in $\chi_{3\omega}'$ appeared at a higher temperature than that in $\chi_{1\omega}'$. It means that domain formation occurs above the Curie temperature, determined by $\chi_{1\omega}'$. In a cyanide-bridged molecule-based magnet with crystallographic chirality, a large nonlinear response has been observed just above the Néel temperature [9], which surely reflects the response of the magnetic domain against the AC field. A similar large nonlinear response was also observed in Cr$_{1/3}$NbS$_2$ in the present study.

![Figure 1](image1.png)

**Figure 1.** Temperature dependences of $\chi_{1\omega}'$ (a) and $\chi_{3\omega}'$ (b) for Cr$_{1/3}$NbS$_2$ at $P = 0$ GPa.

![Figure 2](image2.png)

**Figure 2.** Temperature dependences of $\chi_{1\omega}'$ (a) and $\chi_{3\omega}'$ (b) for Cr$_{1/3}$NbS$_2$ at $P = 3.1$ GPa.
Figure 3 shows the temperature dependencies of $\chi_{3\omega}'$ at $P = 3.1$ GPa, obtained by the four approaches. In Approach 1, the anomaly in $\chi_{3\omega}'$ could not be observed definitely, whereas in Approaches 2-4, it was detected at 108 K with an S/N accuracy of 2.5-3.0. Indeed, Approach 4 yielded the best S/N. A detailed comparison of the four approaches is given in Table 1. For the detection of a minute signal, which is likely to be buried in the $1/f$ noise and the line noise, Approach 4, which calculates the median, yields the best performance.

![Graphs showing temperature dependencies of $\chi_{3\omega}'$ for Cr$_{1/3}$NbS$_2$ at P = 3.1 GPa, obtained by the four approaches.](image)

**Figure 3.** Temperature dependencies of $\chi_{3\omega}'$ for Cr$_{1/3}$NbS$_2$ at $P = 3.1$ GPa, obtained by the four approaches. $\Delta f$ stands for the frequency resolution in FFT.

**Table 1.** Comparison of the four approaches. $N$, the number of wave patterns obtained in the measurement; $N'$, the number of FFTs performed; $n$, the sampling number per one wave for FFT; $f_s$, the sampling ratio; $\Delta f$, the frequency resolution in FFT; S/N, the signal-to-noise ratio in the analyzed data.

|   | $N$ | $N'$ | $n$ | $f_s$ [kHz] | $\Delta f$ [Hz] | S/N |
|---|-----|------|-----|-------------|-----------------|-----|
| No. 1 | 30  | 1    | 2344 | 11.72       | 5.0             | None|
| No. 2 | 30  | 1    | 70320| 11.72       | 0.177           | 2.5 |
| No. 3 | 30  | 30   | 2344 | 11.72       | 5.0             | 2.5 |
| No. 4 | 30  | 30   | 2344 | 11.72       | 5.0             | 3.0 |

The pressure response in Cr$_{1/3}$NbS$_2$ is summarized to discuss the development of a magnetic correlation by the use of both $\chi_{1\omega}'$ and $\chi_{3\omega}'$. The temperatures of the anomaly, obtained from $\chi_{1\omega}'$ and $\chi_{3\omega}'$, are represented by red and blue circles; it was found that the disparity between them is enlarged at $P > 3$ GPa. When we discuss the development of the magnetic correlation at $P = 6$ GPa as an example, the domain formed by short-range correlation is considered to become stable at the temperature of more than 10 K above $T_C$, and this temperature deviation is approximately 1 K at $P = 0$ GPa. We think a helical spin structure was also formed in the short-range domain. This domain is a kind of cluster; namely, prior to the magnetic ordering, and it might be considered to be a Griffiths phase [15] or an inter-domain glass state (if there is a correlation between the domains). At high pressure, the structural defect is induced locally, which might stabilize the short-range domain over the finite temperature
range. If the short-range domain has a helical spin structure, and the pressure response is surely more sensitive to structural stimuli than in a magnetic order without helical modulation. We do not understand in detail why $T_C$ decreases with pressurization, whereas it might be considered that the instability of the helical spin structure under pressure suppresses the $T_C$.

![Graph](image)

**Figure 4.** Pressure dependence of characteristic temperatures for Cr$_{1/3}$NbS$_2$, estimated from the data of $\chi_{1\omega}$ (red) and $\chi_{3\omega}$ (blue). Open and closed marks show the data in the first run ($\leq 3.1$ GPa) and the second run ($\leq 6.0$ GPa), respectively.

5. Conclusion
With the aim of finding a method of observing minute nonlinear magnetic responses, we examined four analytic approaches to the AC SQUID response obtained with a commercial SQUID system: (1) averaging 30 wave-form data and performing one Fourier transformation of the average, (2) connecting 30 data along the time axis and performing one Fourier transformation of the connected data, (3) performing 30 Fourier transformations and calculating the mean value of the 30 resulting analytic values, (4) performing 30 Fourier transformations and calculating the median of the 30 resulting analytic values. For minute signals of the order of $10^{-9}$ emu, the fourth approach yielded the best S/N ratio. In the future, if the nonlinear magnetic susceptibility can be measured with an accuracy of $10^{-9} - 10^{-10}$ emu, the variation of the magnetic properties should be discussed in more detail.

References
[1] Karuzawa M, Ishizuka M and Endo S 2002 *J. Phys.: Condensed Matter* 14 10759
[2] Ishizuka M, Endo S 1999 *Physica* B 265 254
[3] Mito M, Hitaka M, Kawai T, Takeda K, Kitai T and Toyoshima N, 2001 *Japan. J. Appl. Phys.* 40 6641
[4] Takeda K and Mito M. 2002 *J. Phys. Soc. Jpn.* 71 729
[5] Mito M, 2007 *J. Phys. Soc. Jpn.* 76 Suppl. A 182
[6] Ohba M, Kaneko W, Kitagawa S and Mito M, 2008 *J. Am. Chem. Soc.* 130 4475
[7] Mito M, Matsumoto K, Komorida Y, Deguchi H, Takagi S, Tajiri T, Iwamoto T, Kawai T, Tokita M and Takeda K 2009 *J. Phys. Chem. Solids* 70 1290
[8] Tominaga S, Komorida Y, Mito M, Deguchi H, Takagi S, Koyama K, Hamada M, 2009 *J. Phys. Conference Series* 150 052271
[9] Suzuki M 1997 *Prog. Theor. Phys.* 58 1151
[10] Miyako Y, Shikazawa S, Saito T and Yuochunas Y G 1979 *J. Phys. Soc. Jpn.* 46 1951
[11] Fujiki S and Katsura S 1981 *Prog. Theor. Phys.* 65 1130
[12] Mito M, Iriguchi K, Deguchi H, Kishine J, Kikuchi K, Ohsumi H, Yoshida Y and Inoue K 2009
    Phys. Rev. B 79 012406

[13] Miyadai T, Kikuchi K, Kondo H, Sakka S, Arai M and Ishikawa Y 1983
    J. Phys. Soc. Jpn. 52 1394

[14] Piermarini G J, Block S, Barnett J D and Forman R A 1975
    J. Appl. Phys. 46 2774

[15] Griffiths R. B. 1969
    Phys. Rev. Lett. 23 17