Improvement of Reproducibility of Magnetic Moment Detected by a SQUID Magnetometer Through Radial Offset Measurement on a YIG Sphere

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We report here on the reproducibility of measurements on a second-order gradiometer superconducting quantum interference device magnetometer of two different yttrium iron garnet spheres, both having a diameter of 1 mm: 1) the National Institute of Standards and Technology magnetic moment standard reference material (SRM) and 2) a commercial sample. It has been suggested that rotating the sample rod around its axis can move the sample center toward the center of the second-order gradiometer coil. The observed value of the magnetic moment will be theoretically a minimum when the radial offset is 0, and this value will increase in a "quadratic" manner with the radial offset. When the magnetic moment of the SRM was repeatedly measured as a function of rotation angle φ from 0° to 360°, we observed a sinusoidal variation in the measured values. The radial offset dependence of the observed magnetic moment was experimentally confirmed by the measurements of the commercial sphere placed in a hole in several cylindrical containers, wherein the distance between the center of the hole and the center of the container was r. The r-dependence of the minimum from each φ-dependent measurement series is qualitatively consistent with the theoretical curve. When the φ-dependent measurements for the SRM in a capsule were repeated 12× over 21 months, the relative standard deviation of the minimums improved up to 0.1%. Knowledge of these facts will be necessary for the accurate measurement of the magnetic moment of other sample forms (e.g., powders).

Index Terms—**Calibration, reproducibility, superconducting quantum interference device (SQUID), yttrium iron garnet (YIG).**

I. Introduction

A SECOND-ORDER gradiometer superconducting quantum interference device (SQUID) magnetometer, for example, the magnetic property measurement system (MPMS) manufactured by Quantum Design, Inc., is widely used in magnetics research [1]. Matsumoto and Kato [2], Matsumoto and Shimosaka [3]–[5], and Matsumoto and Itoh [6] use this type of magnetometer for quantitative analysis through the "effective magnetic moment method" in the field of analytical chemistry and metrology in chemistry. In [3], a standard reference material (SRM), which has a certified value of the magnetic moment which is metrologically traceable to the International System of Units (SI), was repeatedly measured to calibrate the equipment. The SRM was the National Institute of Standards and Technology (NIST) SRM 2853 "magnetic moment standard-yttrium iron garnet (YIG) sphere." The YIG sphere has the smallest size among NIST's magnetic moment SRMs; so it is the closest to a point dipole. However, the reproducibility on the SQUID magnetometer of the measured values was not good, and its relative expanded uncertainty (coverage factor is 2) was 1.8% (corresponding to a relative standard deviation of 0.9%), as shown in Fig. S1 (supplemental material).

Many researchers have calculated or discussed the errors in magnetic moment measured using the second-order gradiometer SQUID magnetometer [7]–[19]. Specifically, there are three main types of errors on the measured magnetic moment: 1) radial offset; 2) axial offset; and 3) sample shape effect. Among the three types, it was pointed out by Morrison and zur Loye [18] that the radial offset and the sample shape effect can be very significant. The radial offset is the distance between the center of the second-order gradiometer coil and the center of the sample, in a plane perpendicular to the axis through the center of the coil. Some researchers [8], [9], [12], [15] calculated that the observed value of the magnetic moment will be a minimum when the radial offset is 0, and this value will increase in a "quadratic" manner with the radial offset. Software [20] can "correct" raw moment data based on the theory described in [11], considering the radial offset and the sample shape effect. The correction is made on the basis of a "standard" sample, such as a palladium (Pd) cylinder supplied by the manufacturer. However, the Pd cylinder, with a length of 3.8 mm and a diameter of 2.8 mm, is far from a point dipole and its magnetic moment is not traceable to the SI. The Pd cylinder supplied by the manufacturer is neither a primary standard of a National Metrology Institute nor a secondary standard which is traceable to a primary standard (unless this is specifically indicated). Kiss *et al.* [17] reported measurements of $Co_{1.9}Fe_{1.1}Si$ (a Heusler alloy), iron, and nickel in the form of a small piece of an ingot while rotating the sample rod around its axis. Kiss *et al.* [17] also stated that its rotation operation moved the sample center toward the center of the second-order gradiometer coil. The most accurate magnetic moment was viewed as having occurred when the output voltage of the MPMS had the best fit (when regression factor R was closest to unity) to the theory based on an "iterative regression" procedure [9]. Morrison and zur Loye [18] reported measurements (on the MPMS3) of powder samples of Dy_2O_3, Er_2O_3, or Gd_2O_3 in both the "dc measurement mode" and the "VSM mode." The accurate magnetic moment was determined by adjusting the radial offset on the software until the results of both the dc measurement and the VSM measurement coincided with each other.

In this paper, an operation to minimize the error due to the sample's radial offset and its impact on improving the reproducibility will be presented. Good reproducibility can be achieved by assuming that the minimum of the magnetic moment during the rotation of sample rod gives an accurate measurement of the magnetic moment of the sample, i.e., the sample center lies closest to the center of the coil. Two different YIG spheres, both having a diameter of 1 mm, were measured here: 1) the NIST magnetic moment standard and 2) a commercial sample.

II. Experiment

MPMS-7 (Quantum Design, Inc.) with the standard transport and the horizontal rotator option was used for magnetic moment measurements in this study. If the long axis of the cylindrical sample space is in the z-direction, then the horizontal rotator option was used to rotate the sample rod in the ϕ-direction. All measurements were carried out in the dc measurement mode using the iterative regression procedure. The scan length and the number of data points were 4 cm and 32 points, respectively.

The NIST SRM 2853 (YIG sphere) has a certified value of (27.6 ± 0.1) $A \cdot m^2$/kg for the specific magnetization at 298 K in a fixed applied magnetic field strength of 397.89 kA/m (5 kOe). This value has an expanded uncertainty with a coverage factor of 2. The mass was (2.816 ± 0.009) mg [3]. The product of the certified value and the mass was $(7.76 \pm 0.03) \times 10^{-5}$ $A \cdot m^2$. These values also had the expanded uncertainties. The SRM was packed in a cellulose capsule with a nominal diameter of 5.06 mm (Matsuya, MP capsule, No. 4). Another sample, a single crystal YIG sphere (Ferrisphere, Inc.) with highly polished surface and a diameter of 1 mm was used for the measurement of the radial offset.

III. Experimental Results and Discussion

Figs. 1 and 2 show the ϕ-dependences of the magnetic moment of the SRM or the commercial sphere, respectively, at 298 K and in the applied magnetic field of 397.89 kA/m. In Fig. 1, the SRM was mounted inside the cellulose capsule using cotton, and the capsule was inserted in a plastic drinking straw. A cap was attached at the bottom of the straw to prevent the loss of sample. In Fig. 2, the commercial sphere was placed in a hole in a cylindrical polytetrafluoroethylene (PTFE) container inside a quartz tube at distance r between the center of the hole and the center of the container. Ten PTFE containers with different r values were prepared for this study. The commercial sphere was used to avoid contaminating the SRM used in Fig. 1. We assumed that the quality of the YIG sphere in Fig. 2 was the same as that in Fig. 1, as the commercial YIG sphere was manufactured by the company to whom the technology of the SRM YIG sphere was transferred.

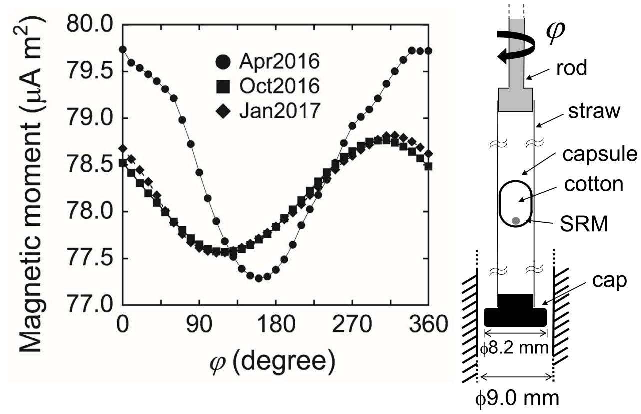

Fig. 1. ϕ-dependences of the magnetic moment for the NIST SRM in a capsule at 298 K at an applied magnetic field of 397.89 $kA \cdot m^{-1}$. Each data point was measured three times in succession, and its typical relative standard deviation was 0.02%–0.005%.

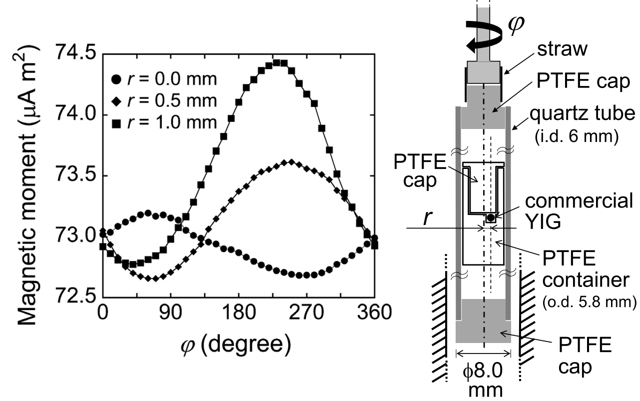

Fig. 2. ϕ-dependences of the magnetic moment for the commercial YIG sphere in one of the custom PTFE containers at 298 K at an applied magnetic field of 397.89 $kA \cdot m^{-1}$. Each data point was measured three times in succession, and its typical relative standard deviation was 0.02%–0.005%.

During the rotation of the sample rod, the center of the sphere can move up to 0.5 mm from the center of the sample space due to the gap between the edge of the cap at the bottom of the plastic straw and the inner diameter of the sample space. When angle ϕ of the sample rod was rotated from 0° to 360°, we observed sinusoidal variations in the measured values of both the samples. In Fig. 1 (April 2016 dataset), the difference between the maximum at 340° and the minimum at 160° is approximately 3.2% of the minimum.

The rotation of the sample rod can move the position of the sphere in both the z-direction and in the xy plane. To determine the influence of any possible movement in the z-direction, i.e., axial offset effect, the SRM was placed in the wider half of the capsule and the other half of the capsule was inverted to "hold" the SRM in place [18]. First, the magnetic moment was measured three times each (and averaged) from 0° to 360° in 10° step, as shown by closed circles in Fig. S2 (supple-

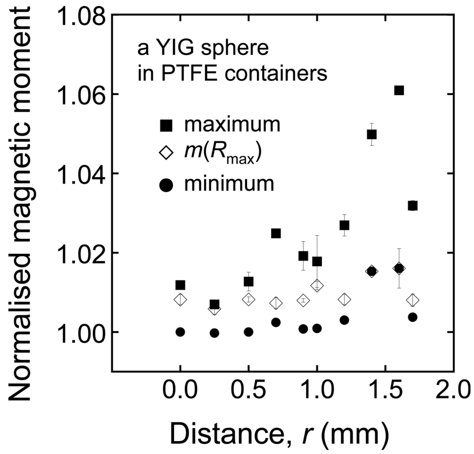

Fig. 3. Radial offset measurement at 298 K using a commercial YIG sphere in the PTFE containers with different r values. The vertical axis is the normalized magnetic moment, i.e., the magnetic moment divided by the minimum magnetic moment at $r = 0$ mm.

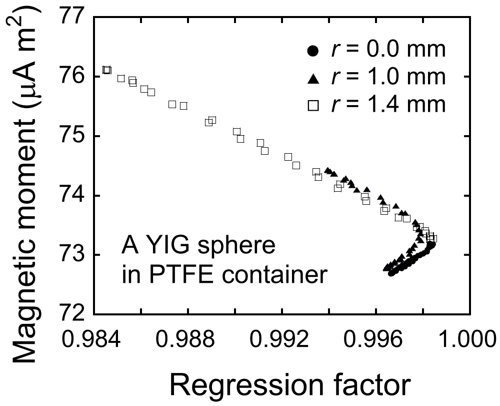

Fig. 4. Correlation of the magnetic moment and the regression factor when the commercial YIG sphere was measured in the PTFE containers. (Representative r values only are shown.)

mental material). Afterwards, the sample was repositioned by initializing the transport to a known position, verifying the signal presence in the full scan length, before centering over the normal scan length using the instrument automatic centering feature. Then, the magnetic moment was measured three times and averaged, as shown by closed squares in Fig. S2. These measurements were carried out at 0°, 50°, 100°, 150°, 200°, 250°, 300°, and 340°, where the sample was removed from the sample space between each angle. The standard deviation of each set of three "repositioned" measurements varied between 1.7×10^{-8} and 3.2×10^{-8} A$\cdot$m^2, which was about 10× larger than those of the original measurement (without repositioning), for unknown reasons. However, the values are within one standard deviation of each other, due to the incorporation of the center position in the fitting equation. Therefore, this result shows that the axial offset may not be significant.

Fig. 3 shows the results of the normalized magnetic moment from the ϕ-dependent measurements of the commercial YIG sphere in the ten PTFE containers with different r values. For each r, the maximum and the minimum of the angular measurements are plotted. The measurements are normalized using the minimum magnetic moment at $r = 0$ mm. The non-normalized magnetic moments of the minimum and the maximum at $r = 0$ mm are 7.267×10^{-5} A $\cdot$ m^2 at 260° and 7.320×10^{-5} A$\cdot$m^2 at 60° in Fig. 2, respectively. The error bars are the standard deviation (1σ) calculated from the repeated ϕ-dependent measurements of the sphere in each container. The relative standard deviations of the minimums and the maximums for $r = 0$ mm are 0.007% and 0.015%, respectively. With increasing r, the minimum is almost constant from 0 to 1.2 mm and then increases for r greater than 1.4 mm. The relative standard deviations of the minimum values for r between 0 and 1.2 mm are 0.007%–0.01%. In contrast, the maximum rapidly increases for r greater than 0.5 mm. The standard deviations of the maximum values are much larger than those of the minimum values.

Miller [8], McElfresh *et al.* [9], Garcia *et al.* [12], and Sawicki *et al.* [15] calculated the theoretical radial offset dependence of the apparent magnetic moment. From the calculated result, the apparent magnetic moment has a minimum when a point dipole is exactly in the center of the coil and increases in an approximately "quadratic" manner with radial offset, due to the changes in the mutual inductance between the sample and the detection coils with the radial position of the sample. In the calculations from [9], for example, the errors are approximately 0.2% at 0.05 mm, 0.7% at 1 mm, 1.5% at 1.5 mm, and 2.7% at 2 mm. The r-dependence of the minimum in Fig. 3 is very similar to the radial offset dependence of the apparent magnetic moment. The radial offset effect also seems to dominate the results of the maximum values.

Using the method from [17], $m(R_{max})$ represents the φ-dependent magnetic moment when the regression factor was the closest value to unity. Fig. 3 also shows $m(R_{max})$ for each r. For r of 1.4–1.7 mm, $m(R_{max})$ is close to the respective minimum value for that r. In the range of 0.7–1.2 mm, $m(R_{max})$ is between the maximum and the minimum values. $m(R_{max})$ at $r = 0$ and 0.5 mm is close to the maximum value. Fig. 4 shows the regression factor dependence of the magnetic moment of the YIG sphere in the PTFE container, for the corresponding r value. For $r =$ 1.4 mm, the magnetic moment decreases linearly while the regression factor (R) increases from 0.984 to 0.998. This agrees with the previous discussion on the radial offset; similar results were seen with the $Co_{1.9}Fe_{1.1}Si$ Heusler alloy (sample size less than 3 mm), where the slope relating the magnetic moment with R was negative, for R values between 0.988 and 0.996 [17]. On the other hand, for $r = 1$ mm, the relationship of the magnetic moment is not one-to-one, but has a "boomerang" shape, for R values of 0.993–0.998. The relationship between R and the magnetic moment for r from 0.5 to 1.2 mm also had a similar "boomerang" pattern. For $r = 0$ mm, the slope relating the magnetic moment and R is positive, for R values of 0.996–0.998. The relationship of $r = 0.25$ mm was also similar. In summary, as shown in Figs. 3 and 4, the relationship between R and the magnetic moment is as expected for a "large" sample or for the small YIG sphere when the radial offset r is greater than 1.4 mm. The YIG sphere at $r = 0$ mm shows the smallest difference between the maximum and the minimum in the ϕ-dependent measurement. However, the relationship of $m(R_{max})$ and the magnetic moment is opposite to $m(R_{max})$

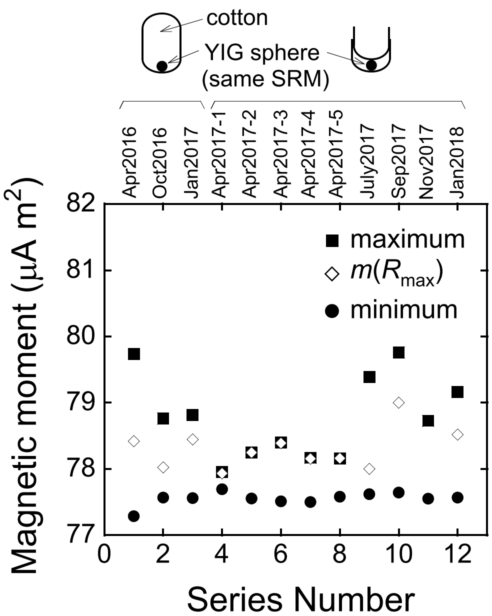

Fig. 5. Long-term stability of the magnetic moment of the SRM at 298 K. The same measurements as Fig. 1 were repeated over 21 months. The vertical axis is the minimum or the maximum of the observed magnetic moment determined from the ϕ-dependence of the magnetic moment.

close to the maximum value. This could be caused by an imperfection in the fitting function [1] obtained from the Biot–Savart law assuming a point dipole although the YIG sphere was smaller than the alloy sample.

Fig. 5 shows the minimum values and the maximum values of the SRM in a capsule (the same method as used in Fig. 1) when the ϕ-dependent measurements were carried out over a period of time from Apr. 2016 to Jan. 2018. Reproducibility of the minimum was much better than that of the maximum and of $m(R_{\max})$. The average and its relative standard deviation of the minimum values over the period were 7.773×10^{-5} A $\cdot$ m^2 and 0.12%, respectively. This demonstrates the possibility of a high-accuracy calibration of the SQUID magnetometer using the YIG sphere SRM. In the five measurements in Apr. 2017 (series number 4–8), $m(R_{\max})$ and the maximum for each series number were consistent with each other and the differences between the maximum and the minimum were relatively smaller than those of the other months. The results from the Apr. 2017 were similar to the results for r from 0 to 0.25 mm and show that the SRM had little movement in the plane perpendicular to the z-direction. In practice, in Apr. 2017, a new straight sample rod for the standard transport was used, while the sample rods used in other months were slightly bent. Therefore, the rotation of the sample rod and use of the minimum value as the most accurate value is also an effective measurement technique to obtain good reproducibility, independent on the straightness (or not) of the rod. Each sinusoidal variation of the magnetic moment in Fig. 1 is caused by a change in the radial offset while rotating the sample rod, and the "amplitude" of the sinusoidal variation depends on the degree of straightness of the rod. The non-systematic data in an angle range of 180°–360° measured in Apr. 2016 in Fig. 1 might have also been due to a lack of straightness of the rod.

IV. Conclusion

The measurements of the ϕ-dependence both by rotating the sample rod and by using the minimum value from the ϕ-dependent measurement have successfully improved the reproducibility of the magnetic moment detected by the second-order gradiometer coil, to a relative standard deviation of 0.12%. The long-term stability was also considered (over 21 months). The reproducibility is much better than the relative expanded uncertainty of the certified value of the SRM, 0.29%. Using this method in conjunction with the YIG sphere SRM will make high-precision calibrations and long-term stability monitoring of the SQUID possible if the uncertainty of SRM can be decreased in the future. Finally, the experimental data accounting for the radial offset effect will be useful for the measurements of various samples in other forms (e.g., powders).

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