Simple Correction for the Sample Shape and Radial Offset Effects on SQUID Magnetometers: Magnetic Measurements on Ln_2O_3 ($Ln = Gd, Dy, Er$) Standards

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Abstract: An increased focus on magnetic measurements of oriented single crystals, thin films, and magnetically dilute systems has led to a demand for the measurement of weak magnetic moments. This level of sensitivity and precision can be achieved on SQUID magnetometers by decreasing the size of the detection coils. However, the smaller detection coils can amplify two errors in the magnitude of the measured moment, the sample shape and radial offset effects, which were small and typically unaccounted for on previous magnetometers. We report a simple method to determine the radial offset of a sample by taking advantage of the two basic scan modes, DC and lock-in, typically used on magnetometers. This technique allows for the correction of the sample shape and radial offset effects in order to obtain the true moment of a sample. To show the efficacy of this technique, we report the magnetic properties of Ln_2O_3 ($Ln = Gd, Dy, Er$).

Keywords: Magnetic measurements; SQUID Magnetometers; Sample shape; Radial offset; Moment correction

1. Introduction

Magnetic property measurement systems typically utilize a second order gradiometer inductively coupled to a superconducting quantum interference device (SQUID) in order to measure the magnetic moment of a sample. In such a setup, a magnetic sample moves through the gradiometer and induces a current which is detected by the SQUID coils and is proportional to the moment of the sample.^{1, 2} In an ideal case, the magnetic sample is a dipole which vibrates on the center axis of the gradiometer and whose volume is a few percent of the volume of the detection coils. In such a case, the true moment of the sample is measured.³ However, when the sample is not a dipole or is larger compared to the detection coils, the moment measured by the magnetometer may not be the true moment.

In recent years, condensed matter research has seen an increased demand for the measurement of weak magnetic moments. The advent of modern diffraction techniques, with microfocused X-ray beams and the ability to collect neutron diffraction data on sub 1 m³ crystals, has led to an emphasis on single crystal growth⁴ and an increased demand for magnetic measurements on small, oriented single crystals. Furthermore, an increased focus on weakly magnetic systems, such as thin films, and low field measurements, such as for AC susceptibility, has enhanced the need for the measurement of small moments. The high sensitivity and precision needed for these measurements can be achieved with SQUID magnetometers by shrinking the size of the detection coils, and in turn, sample chamber and scan lengths.¹ Along with higher precision, the smaller sample chambers can also allow for more rapid cooling and temperature stabilization.⁵ While providing many advantages, the smaller detection coils, relative to the sample size, can amplify two errors in the magnitude of the moment^{6, 7} that were small, rarely noticed, and typically unaccounted for in previous magnetometers.

The first increase in the measurement error occurs due to the sample shape effect.⁷ This effect can be mathematically calculated and has been for many common shapes using programs such as MATHCAD, MATHEMATICA, and MAPLE.^{3, 8} Mathematically, a point charge or sphere has no sample shape effect and yields the true moment, whereas any other shape yields either a higher or lower moment.³ Quantum Design offers a program which calculates the sample shape effects for any cylinder, thin film, or rectangular prism.⁹ However, this program is specific to their MPMS 3 as the MPMS 3 is calibrated to a Pd cylinder that has a height of 3.8 mm and a width of 2.8 mm. As a result, a cylinder of the same shape has no sample shape effects on the MPMS 3, while any other shape does.^{7, 10}

The second increase in the measurement error occurs due to the sample's radial offset. A sample that vibrates in the radial center of the gradiometer generates the true moment. As the vibrational axis of the sample moves off the center of the gradiometer (for example because the straw or other sample holder is slightly curved), the measured moment increases.⁶ Although the effect of this radial offset can be calculated mathematically if the offset value is known,³ the exact offset value cannot be measured. The data can be improved by rotating the sample into the "minimal radial offset" location, determined by rotating a sample within the gradiometer and finding the orientation that generates the smallest moment. Unfortunately, this technique only finds the minimal offset, not the zero offset. Cellophane tape guides of approximately the diameter of the sample chamber can also be attached to the sample holder to reduce the radial offset,¹¹ but again, this method does not guarantee zero radial offset. Furthermore, the friction produced by these guides can inhibit temperature stability at low temperatures (< 10 K).

Two types of scan modes are typically used on magnetometers. The first method, DC scans, moves the sample completely through the detection coils and fits the entire resulting

voltage curve in order to obtain the sample moment. The second method uses a lock-in technique, such as RSO and VSM scans, which have much smaller scan lengths and only look at the section around the maximum of the voltage curve. It is important to note that a VSM scan is different from the measurement performed on a vibrating sample magnetometer, with the prior measuring the magnetic flux in the detection coil¹⁰ and the latter measuring the change in flux in a coil.¹² Both the sample shape and radial offset effects increase in magnitude as the scan length is decreased and typically result in an over determination of the moment (some sample shapes can lead to an under determination of the moment).¹⁰ These effects are far more pronounced in lock-in measurements than in DC measurements, yet even with DC scans the error due to these effects can be appreciable. Herein, we present a simple technique to correct for both of these effects. To show the method's efficacy, we report the magnetic susceptibilities of three rare earth oxides, Gd_2O_3 , Dy_2O_3 , and Er_2O_3 . This method allows for the measurement of the true moment of a sample and can make lock-in scans as accurate as the slower and less precise DC scans.

2. Materials and Methods

Gd_2O_3 (powder- 99.999% REO), Dy_2O_3 (powder- 99.9% REO), and Er_2O_3 (powder- 99.9% REO) were used as received. While these values pertain only to the purity of the rare earth with respect to other rare earths, the certificates of analysis from the manufacture, Alfa Aesar, indicated that the sum of all metal impurities were less than 0.1% for each rare earth oxide. Furthermore, powder X-ray diffraction data (not shown), collected on a Rigaku Ultima IV diffractometer with a $Cu\ K\alpha$ source ($\lambda = 1.54056\text{ \AA}$) and a DTex detector, showed no evidence of any non-rare earth oxide phases. The rare earth oxides, massing 35-45 mg, were loaded into gelatin capsules for measurement. The rare earth oxide was placed in the wider half

VSM scan mode, combining the measurement speed of a VSM with the sensitivity of the SQUID.⁵ Data were collected using the temperature sweeping zero-field-cooled (ZFC) conditions at 1000 Oe. Data were collected in

of a gelatin capsule and the other half of the capsule was inverted into it to keep the powder in place. The two halves were taped together with a strip of Kapton tape and inserted into a clear plastic straw. Accurate sample masses were obtained by weighing by difference on a balance sensitive to 0.01 mg. Sample dimensions were measured using digital calipers. The samples were approximated as cylindrical with the diameter being the width of the gelatin capsule and the height being the height from the bottom of the capsule to the top of the sample.

Magnetic susceptibility data were collected on a Quantum Design MPMS 3 SQUID magnetometer. The MPMS 3 has a small sample chamber and pickup coils allowing for high precision measurements, $\leq 10^{-8}$ emu sensitivity, and fast cool down rates, 300 K to 1.8 K stability in under 30 minutes. Furthermore, it has a

Figure 1. Evolution of the magnetic susceptibility data through the correction process for Dy_2O_3 showing a) raw data, b) shape corrected data and c) shape and radial offset corrected data where the radial offset correction factor was varied until the 30 K DC and VSM moments were equal.

rapid the high were collected mode under from 30 -300 K the DC scan

mode with 30 mm scan lengths and 5 second averaging and in the VSM mode with 5 mm scan lengths and 2 second averaging. The magnetic field was set to 30,000 Oe and oscillated back to 0 Oe before each data collection to ensure that the field was consistent between measurements. Raw moment data were corrected for sample shape and radial offset corrections using the MPMS 3 Sample Geometry Simulator.⁹

3. Results and Discussion

Figure 1 shows the magnetic susceptibility data of Dy₂O₃, which is summarized in Table 1. As can be seen in Figure 1a, when no corrections are applied the VSM data is considerably higher than the DC data. Fitting the inverse susceptibility with a Curie-Weiss fit yields effective moments of 11.24(3) μ_B/Dy (DC) and 11.76(3) μ_B/Dy (VSM), both of which are well above the expected calculated moment of 10.65 μ_B/Dy . When a sample shape correction is applied, the agreement between the two susceptibilities improves, as shown in Figure 1b, but still do not match. The effective moments of 10.94(3) μ_B/Dy (DC) and 11.17 μ_B/Dy (VSM) are also in better agreement, but are nonetheless still higher than the expected calculated moment of 10.65 μ_B/Dy .

TABLE 1. Magnetic data through the correction process for Dy₂O₃.

Correction Applied	DC Correction Factor	DC μ_{eff} (μ_B/Dy)	VSM Correction Factor	VSM μ_{eff} (μ_B/Dy)	μ_{calc} (μ_B/Dy)
None	-	11.24(3)	-	11.76(3)	10.65
Shape (2.8 mm H x 5 mm D)	1.057	10.94(3)	1.108	11.17(3)	10.65
Shape + Radial Offset (1.70 mm)	1.112	10.66(3)	1.215	10.67(3)	10.65

As the DC and VSM measurements were performed on the same sample under the same conditions they should have identical moments. The three factors that can lead to a deviation in

the moments are the shape effects, the radial offset, and the axial offset. There should be essentially no axial offset as all samples were axially centered at 30 K and kept centered using auto-tracking, a method which uses the thermal expansion coefficients of the sample holder to predict where the sample is at all temperatures. Furthermore, the raw DC scans are fit with a free center, DC Moment Free Fit, meaning an axial offset of the sample would not affect the measured moment. As a result, any axial offset would lead to a smaller VSM moment, which is not what is observed in Figure 1b. Since the shape correction has already been applied, it is reasonable to assume that any remaining deviation between the VSM and DC data is caused by a radial offset.

While the radial offset of the sample cannot be measured directly, it can be determined through trial and error by adjusting the radial offset until the VSM and DC data overlap. The best radial offset was found by adjusting the radial offset in 0.05 mm increments and choosing the radial offset with the minimum difference in the 30 K VSM and DC moments. For Dy_2O_3 , this radial offset was found to be 1.70 mm. Figure 1c shows the susceptibilities after this radial offset is applied. The two susceptibilities overlap and the observed effective moments of $10.66(3) \mu_B/\text{Dy}$ (DC) and $10.67(3) \mu_B/\text{Dy}$ (VSM) are almost identical and are in excellent agreement with the expected calculated moment of $10.65 \mu_B/\text{Dy}$.

In order to correct for the radial offset effect using the method outlined in this manuscript, two measurements with different correction factors must be made. The correction factor for the DC scan only changes slightly with increased scan length making it very difficult to determine an accurate radial offset using only DC scans.¹⁰ There is a much more pronounced change in the correction factor when changing the scan length of the VSM scan,¹⁰ so it should be possible to determine the radial offset using two VSM scans of different lengths. The

combination of the DC and VSM scans is used in this manuscript as they provide the most disparate correction factors and therefore, allow for the most accurate determination of the radial offset. While in this manuscript, the two data points are collected at 30 K, they can be collected at any temperature at which the signal is sufficiently greater than the background to produce a well formed DC voltage curve. As a result, collecting the data required for the correction can typically be easily inserted into a data collection and takes under one minute.

TABLE 2. Corrected magnetic data for Ln_2O_3 ($Ln = Gd, Dy, Er$).

Sample	Mass (mg)	Cylinder Size (H x D)	Radial Offset (mm)	DC θ_{CW}^a (K)	DC μ_{eff}^a (μ_B/Ln)	M_{calc} (μ_B/Ln)
Dy ₂ O ₃	44.14	2.8 x 5	1.70	-19.5(4)	10.66(3)	10.65
Er ₂ O ₃	36.77	2.4 x 5	1.30	-14.2(3)	9.54(3)	9.58
Gd ₂ O ₃	41.95	3.1 x 5	1.75	-13.4(3)	7.85(2)	7.94
Gd ₂ O ₃	41.04	3.1 x 5	1.00	-13.8(3)	7.89(2)	7.94
Gd ₂ O ₃	41.04	3.1 x 5	1.25	-13.7(3)	7.88(2)	7.94
Gd ₂ O ₃	38.46	3 x 5	0.90	-13.2(3)	7.84(2)	7.94
Gd ₂ O ₃ (VSM Powder Holder)	22.70	2.65 x 2.6	0.95	-13.2(3)	7.86(2)	7.94

^a Error bars based on the standard deviation of the four Gd₂O₃ gelatin capsule in straw samples

To test the efficacy of this method, magnetic susceptibility data was also collected on Er₂O₃ and Gd₂O₃, two lanthanide cations that have well known effective moments. As shown in Table 2, Er₂O₃ had a shape of 2.4 mm H x 5 mm D and was found to have a radial offset of 1.30 mm. Using these corrections, the DC effective moment was found to be 9.54(3) μ_B/Er , which is in very good agreement with the calculated moment of 9.58 μ_B/Er . Four sets of data were

collected on three samples of Gd_2O_3 . While the radial offsets varied from 0.9 mm to 1.75 mm, all data sets are in excellent agreement with an average effective moment of $7.87(2) \mu_B/\text{Gd}$ and an average Curie-Weiss temperature of $-13.5(3) \text{ K}$. This moment is somewhat smaller than the expected $7.94 \mu_B/\text{Gd}$, but is in very good agreement with the moment of $7.86(5) \mu_B/\text{Gd}$ previously observed on an MPMS XL magnetometer.¹³

Finally, in order to study the appropriateness of the cylindrical gelatin capsule approximation, a sample of Gd_2O_3 was loaded into a VSM Powder Holder. This sample was a true cylinder with dimensions 2.65 mm H x 2.6 mm D. Comparing the 30 K moments led to a radial offset of 0.95 mm and a DC scan effective moment of $7.86(2) \mu_B/\text{Gd}$. The excellent agreement between this moment and the average moment of $7.87(2) \mu_B/\text{Gd}$ for the gelatin capsule samples supports that approximating the gelatin capsule as a cylinder is reasonable.

4. Conclusions

The increased demand for the measurement of weak magnetic moments has led to the need for more precise magnetometers with smaller detection coils than previous generation instruments. However, due to the smaller sample chamber, pickup coils, and scan lengths in these new instruments, the shape effects and radial offset effects, which were previously typically small enough to be ignored, are now often large enough to require a correction to the collected data. We present a simple and effective method for determining the radial offset and correcting for these effects. The shape correction factor can be calculated based on the sample shape. Any remaining difference between the DC scan and VSM scan data is due to the radial offset, which can then be determined and corrected for. This simple method allows for the measurement of the true moment of a sample and can make lock-in scan modes, such as VSM and RSO scans, as accurate as the slower and less precise DC scans.

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References

1. R. L. Fagaly, Rev. Sci. Instrum. **77**, 101101 (2006).
2. M. McElfresh, Fundamentals of Magnetism and Magnetic Measurements Featuring Quantum Design's Magnetic Property Measurement System, *Quantum Design*, Available at <http://www.qdusa.com/sitedocs/appNotes/mpms/FundPrimer.pdf>
3. P. Stamenov and J. M. D. Coey, Rev. Sci. Instrum. **77**, 015106 (2006).
4. D. E. Bugaris and H.-C. zur Loye, Angew. Chem. Int. Ed. **51**, 3780-3811 (2012).
5. MPMS 3 Product Description, *Quantum Design, Inc.*, Available at https://www.qdusa.com/sitedocs/productBrochures/1500-102_revC0.pdf
6. Application Note 1500-010, *Quantum Design, Inc.*, 06/01/2010. Available at <https://www.qdusa.com/pharos/>
7. Application Note 1500-015, *Quantum Design, Inc.*, 10/04/2010. Available at <https://www.qdusa.com/pharos/>
8. U. Außerlechner, P. Kasperkovitz and W. Steiner, Meas. Sci. Technol. **9**, 989 (1998).
9. MPMS 3 Sample Geometry Simulator, *Quantum Design, Inc.*
10. D. Hurt, S. Li and A. Amann, IEEE Trans. Magn. **49**, 3541-3544 (2013).
11. MPMS Application Note 1014-201, *Quantum Design, Inc.*, 11/01/2000. Available at <https://www.qdusa.com/pharos/>
12. D. O. Smith, Rev. Sci. Instrum. **27**, 261-268 (1956).
13. S. L. Bud'ko and P. C. Canfield, J. Magn. Magn. Mater **299**, 281-287 (2006).

Graphical Abstract