Reducing systematic errors in measurements made by a SQUID magnetometer

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A simple method is described which reduces those systematic errors of a superconducting quantum interference device (SQUID) magnetometer that arise from possible radial displacements of the sample in the second-order gradiometer superconducting pickup coil. By rotating the sample rod (and hence the sample) around its axis into a position where the best fit is obtained to the output voltage of the SQUID as the sample is moved through the pickup coil, the accuracy of measuring magnetic moments can be increased significantly. In the cases of an examined Co1.9Fe1.1Si Heusler alloy, pure iron and nickel samples, the accuracy could be increased over the value given in the specification of the device. The suggested method is only meaningful if the measurement uncertainty is dominated by systematic errors – radial displacement in particular – and not by instrumental or environmental noise.

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1. Introduction

Recently, we encountered a problem of measuring the saturation magnetic moments of some Heusler alloys [1] with the help of a SQUID magnetometer. These samples are pieces of ingots of irregular shape with dimensions below 3 mm, which have high magnetic moments in the range of 0.5–1.2 emu. Since the contribution of the sample holder is negligible, a high accuracy of the measured moment is expected. However, we obtained a relatively big distribution in the measured moments (deviations up to 2%) when the same sample was repeatedly dismounted and remounted. The accuracy is crucial for the confirmation or rejection of the half-metallic nature of a given Heusler alloy [2,3], and also the non-monotonic composition dependence reported for the saturation magnetic moment of some Heusler alloys series [4–6], which cannot be explained by any theoretical models, may indicate the presence of large systematic errors.

The superconducting quantum interference device (SQUID) is a magnetometer with high sensitivity, and is widely used for the magnetic characterization of a great variety of materials. The high sensitivity is very important when studying samples with one or more dimensions in the nanometer range, i.e. ultrathin films [7] or nanoparticles [8]. There are several articles in the literature which discuss the possible sources of experimental errors in case of measurements by a SQUID magnetometer [9–14]. These papers mainly focus on possible artifacts originating from the small magnetic moment of the sample. Stamenov and Coey [9] and Sawicki et al. [10] describe in detail the theoretical background of magnetization measurements using a second-order gradiometer coil, which is the case in a SQUID magnetometer. Usually the sample is considered to be an ideal dipole and the output voltage of the SQUID obtained as the sample is moved through the second-order gradiometer coil is fitted to the theoretical curve. Corrections to the results of this usual measuring procedure are given [9,10] for the size, shape, position and orientation of the sample, nonuniform magnetization distribution as well as tilted moments (magnetic anisotropy). For our purpose it is important to note that a typical imperfection of the sample mounting occurs when the sample is radially displaced from the rotation axis of the gradiometer coil. In this case the measured magnetic moment monotonously increases up to a distance of 6 mm irrespective of the fitting procedure used [9,13,14]. Such a source of systematic error can arise from the irregular shape of the sample as well as from a slight distortion of the straw generally used to position the sample.

Our aim is to test if this type of systematic error can explain the big distribution of the moments observed for our Heusler-alloy samples with high magnetic moments. For this reason, measurement series have been performed on samples with largely different magnetic moments by repeatedly mounting and dismounting them. First we report the distribution of the measured magnetic moments for a Pd reference sample. Then we analyze the distribution of the data in case of a Heusler-alloy sample and show that they contain a systematic error as compared to the Pd sample.

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We suggest that this systematic error is caused by the radial displacement of the sample and thus a simple method of rotating the sample rod around its axis is proposed to move the sample as close as possible to the gradiometer center. Finally, we check the applicability of this procedure and the absolute accuracy of the device for pure Fe and Ni by effectively rotating the sample rod into well defined positions.

Though the statements of this paper are based on measurements made by a commercial SQUID magnetometer (Quantum Design magnetic property measurements system MPMS 5S) equipped with a second-order gradiometer pickup coil, they may be valid also for any other induction-based magnetometer. The procedure apparently doubles the accuracy of the SQUID magnetometer for our Heusler-alloy sample, as compared to that given in the specification of MPMS 5S.

2. Experimental

Measurements on four different samples were performed on a commercial SQUID magnetometer (Quantum Design MPMS 5S): (1) a Pd reference sample in the form of a cylinder supplied by Quantum Design for calibration (Pd - 553 with a mass of 0.2682 g); (2) a Co_{0.9}Fe_{1.1}Si type Heusler alloys in the form of a small piece of ingot (with a mass of 7.409 ± 0.005 mg) produced by induction melting of the pure constituent elements in a water-cooled copper surface; (3) a pure Fe reference sample (with a mass of 3.659 ± 0.005 mg) taken from a 99.99% purity Fe ingot supplied by Alfa Inc. and (4) a pure Ni reference sample (with a mass of 16.303 ± 0.005 mg) taken from a 99.9% purity Ni ingot supplied by the same company. The shape of the last three samples can be approximated as an ellipsoid with some irregularities in the surface. All four samples have dimensions below 3 mm; therefore they can be regarded as ideal dips with respect to the size of the pickup coil.

The SQUID magnetometer [15] was equipped with longitudinal pickup coils. The Pd sample was measured in the original fused-silica tube supplied by Quantum Design. The other samples were fixed by vacuum grease of type Apiezon M inside a cylindrical teflon sample holder in order to prevent the rotation of the sample under a magnetic field. The sample holder was centered in a usual measuring straw by wrapping a kapton ribbon around it. For all measurements the DC option (4 cm of sample movement except some cases indicated explicitly) of the MPMS was used with a servo transport mechanism except some cases (which will be indicated explicitly) when the standard stepping transport mechanism was applied. For the calculation of the magnetic moment, an iterative regression procedure was used to find the best fit to the output voltage of the SQUID as the sample (considered to be an ideal magnetic dipole) was moved through a second-order gradiometer superconducting pickup coil. The iterative regression procedure was based on a nonlinear least-squares regression which was characterized by a regression value $R$ (being unity for a perfect fit). This approach can account for an offset and a linear drift of the output voltage (after these corrections it is called detrended voltage) giving also a correction for small misdisplacements of the sample along the axis of the gradiometer [16].

3. Results

3.1. Pd sample

The manual [15] of the MPMS 5S SQUID magnetometer specifies the absolute accuracy of the device as 1%. Fig. 1 shows the distribution of the magnetic moments of the Pd reference sample (columns) measured in 1 kOe at 298 K in the period between 1998 and 2012. (Before every measuring period, the calibration of the device was checked).

The number of data is not too big, which might explain that the distribution has a maximum slightly below the mean value. The literature value given by Quantum Design [15] for absolute calibration ($m_{lu}=1.40805 \times 10^{-3}$ emu) is indicated by an arrow, corresponding roughly to the maximum of the distribution.

From the measured individual magnetic moments ($m_i$), the mean value $m = \frac{\sum m_i}{n} = 1.4099 \times 10^{-3}$ (i = 1 to n) and the sample standard deviation $\sigma_{n-1} = \sqrt{\frac{\sum (m_i - \bar{m})^2}{n-1}} = 6.6184 \times 10^{-3}$ (i = 1 to n) were calculated where $n=17$ is the number of measuring points. Using these statistical parameters, a Gaussian distribution function

$$p = \frac{1}{2\sigma_{n-1}\sqrt{\pi/2}} \exp\left(\frac{-m^2}{2\sigma_{n-1}^2}\right)$$

is displayed in Fig. 1 (line) where $m$ is the measured magnetic moment. The top scale of Fig. 1 shows the relative deviation of the moments (in %) from the mean value.

As seen from Fig. 1, the distribution of the measuring points can be approximated by a Gaussian distribution with a half-width of about 1%. It means that the probability that the exact magnetic moment should be within an interval of 1% is 68% (± $\sigma_{n-1}$). Requiring an almost perfect coincidence of 95%, the error margin should be doubled to 2% (± 2$\sigma_{n-1}$). The literature value coincides with the maximum of the measured distribution and with the fitted Gaussian curve (Fig. 1) well within these error limits, indicating that the systematic errors are smaller than the statistical ones.

3.2. Sample of a Heusler alloy (Co_{0.9}Fe_{1.1}Si)

A quite different non-Gaussian moment distribution is obtained for the Co_{0.9}Fe_{1.1}Si Heusler-alloy [1] sample as shown in Fig. 2. The saturation magnetization $M_0$ was calculated by fitting (between 2 and 5 T) the magnetization $M$ vs. magnetic field $H$ curve measured at 5 K to the expression for the law of approach to

![Fig. 1. Normalized probability distribution of the magnetic moment of a Pd reference sample measured in 1 kOe at 298 K by a SQUID magnetometer during the period 1998 and 2012 (columns). The line is a Gaussian distribution function with parameters obtained from statistical calculations (see text). The arrow shows the literature value [15]. The top scale shows the relative deviation of the moments (in %) from the mean value.](https://example.com/fig1.png)
The saturation magnetization measured at 5 K and 5 T ($M_{S,5K,5T}$), which is a model independent quantity, was also used to characterize the saturation magnetization. The corresponding magnetic moments ($m_0$ and $m_{S,5K,5T}$) are calculated from $M_0$ and $M_{S,5K,5T}$ respectively, and refer to a formula unit.

The difference between $m_0$ and $m_{S,5K,5T}$ is within 0.01–0.02 $\mu_B$, therefore only $m_{S,5K,5T}$ is displayed in Fig. 2. The most probable saturation magnetic moment (maximum of the moment distribution) is 5.83 $\mu_B$. However, there are measured points almost evenly distributed within an interval of about 3% above the most probable values. This hints at a huge systematic error compared to the statistical one, which increases the measured magnetic moment. It could be observed that the smaller the measured magnetic moment, the higher the quality of the fit which is clearly seen in the MultiVu program supplied by Quantum Design. We suggest that the hidden parameter should be the rotation angle of the sample rod (and hence the sample) which was not systematically controlled when the same sample was repeatedly dismounted and remounted. The quality of the fit is characterized quantitatively by a regression value that is given by the program for every measuring point. The regression value changes very little ($<0.1\%$) in different points of the $M$–$H$ curve at a given temperature (except for small moments in $H=0$). Therefore, a magnetization curve at a given temperature (hence each saturation moment derived from it) can be related to a regression value. Fig. 3 shows the measuring points plotted in Fig. 2 as a function of the regression value.

The correlation between saturation magnetization (saturation moment) and regression is evident. It is clearly seen that the apparently different values of the saturation moments obtained for Co$_{1.9}$Fe$_{1.1}$Si is an artefact related to the differences in the regression value.

It is worth noting that a similar correlation between the saturation magnetization and the regression value does not exist for the Pd sample, as shown in Fig. 4. It is also remarkable that the overwhelming majority of the regression values lie in the range of $R > 0.995$ and within the experimental uncertainty. Fig. 1 shows no observable sign of systematic error (the Gaussian distribution is close to symmetric) for the Pd sample in contrast to the case of the Heusler alloy. The $\sim 1\%$ full width at half maximum of the distribution is in line with the accuracy given in the specification of the device.

Applying what we have learnt above about the relationship between saturation magnetization and regression value (Fig. 3) for the Heusler-alloy sample, we measured a pure Fe sample, whose saturation magnetization is well-known, as a function of the rotation of the sample rod. Here we used the standard stepping transport mechanism to rotate the sample rod directly from outside. Deliberately, we measured the detailed magnetic-field dependence in two rotation-angle positions of the sample rod: (1) one giving the best regression value ($R=0.9974$) and (2) one with the worst value ($R=0.9893$). The results are shown in Fig. 5.

The saturation magnetization $M_0$ ($M_{S,5K,5T}$) for pure Fe obtained in the best-$R$ and worst-$R$ cases are $221.6 \pm 0.3$ emu/g ($220.8$ emu/g) and $227.1 \pm 0.3$ emu/g ($226.8$ emu/g), respectively. (Here, in order to calculate $M_0$, the fits to the law of approach to saturation were performed between 1 and 5 T.) In the best-$R$ case $M_0$ falls well within the range of the literature values ($221.17$–$222.0$ emu/g). In the best-$R$ case $M_0$ ($M_{S,5K,5T}$) is about 2% (3%) smaller than in the worst-$R$ case and they agree with the literature value within 0.2% (0.5%) and 3% (2%), respectively. The inset shows the SQUID voltage (total coupled flux) as a function of the sample position due to the sample movement through the second-order gradiometer pickup coil for the best-$R$ (squares) and worst-$R$ (dots) case, measured at 5 K and 5 T, together the corresponding fits (solid and dashed lines, respectively). The difference between the measuring points and the corresponding fit is also shown for the two cases (thick solid and
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further complicates the situation. In order to estimate experimen-
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measured a pure Ni sample, the same way as it had been done
indicate that the correlation found between the magnetization and
magnetometer in case of the repeated dismounting and remount-
ing of the Heusler alloy sample (Fig. 3) can be due to the rotation
angle position, determining the absolute accuracy of the SQUID
magnetometer.

3.4. Ni sample

As mentioned above, the systematic errors associated with the
radial displacement of the sample (assuming that there is no radial
component of the magnetic moment measured) can be calculated
theoretically [9] resulting in a monotonous increase of a few
percent of the moment up to a distance of 6 mm. The presence
of a radial component, e.g. if the sample is not properly saturated,
further complicates the situation. In order to estimate experimen-
tally the effect of the latter source of systematic errors, we
measured a pure Ni sample, the same way as it had been done
for pure Fe, since Ni can be more easily saturated than Fe.
Moreover, in addition to the usual 4 cm sample-movement length,
a length of 8 cm was used in order to reach sample positions
where the signal approaches zero. The results are shown in
Figs. 6 and 7.
The saturation magnetization \( M_0 \) (\( M_{b,5K,T} \)) for pure Ni obtained
in the best-\( R \) (\( R=0.9975 \)) and worst-\( R \) cases (\( R=0.9797 \)) are:
58.6 \pm 0.1 \text{emu/g} (58.8 \text{emu/g}) and 61.5 \pm 0.1 \text{emu/g} (61.6 \text{emu/g}),
respectively, for the sample movement of 4 cm. (Here also as for
pure Fe, in order to calculate \( M_0 \), the fits to the law of approach
to saturation were performed between 1 and 5 T). The same values
for the sample movement of 8 cm are (best-\( R \) case: \( R=0.9980 \),
worst-\( R \) case: \( R=0.9801 \)): 58.6 \pm 0.1 \text{emu/g} (58.8 \text{emu/g}) and
61.1 \pm 0.1 \text{emu/g} (61.2 \text{emu/g}), respectively. In the best-\( R \) case \( M_0 \)
falls well within the range of the literature values (57.6–59 \text{emu/g}
[18]). The saturation magnetization measured for the worst-\( R \) case
is about 5\% higher than that for the best-\( R \) case and the latter is
close to the literature value. The very similar results obtained for
pure Fe and Ni show that the systematic errors caused by a
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pure Fe and Ni show that the systematic errors caused by a
possible incomplete saturation of the magnetic moment can be
neglected.

4. Discussion

The results obtained for the pure Fe and Ni sample clearly
indicate that the correlation found between the magnetization and
the regression value of the fit to the output voltage of the SQUID
magnetometer in case of the repeated dismounting and remount-
ing of the Heusler alloy sample (Fig. 3) can be due to the rotation
angle dependence of the measured magnetic moment. This finding
suggests a method to increase the absolute accuracy of the
measurements performed by a commercial SQUID magnetometer.
The method is to rotate the sample rod along its long axis until the
best fit is obtained to the output voltage of the SQUID as the
sample is moved through the second-order gradiometer superconducting pickup coil. According to our experience, it is easy to attain regression values in the range of $0.999 < R < 0.998$. In this case, as can be seen in Fig. 3, the values fall within an interval of $\pm 0.03 \, \mu B$ for the studied Co$_{1.9}$Fe$_{1.1}$Si type alloy. Thus, an accuracy of $w = 2 \sigma_{n-1} = 0.5\%$ can be reached in the absolute value of the magnetic moment which is two times better than the specification given by Quantum Design.

This finding is easily explained in the framework of theoretical calculations [9,10,13,14] according to which the magnetic moment shows an apparent increase when the sample is radially displaced from the rotation axis of the second-order gradiometer coil and the usual fitting procedures are applied. The distortion of the SQUID voltage can be calculated for special cases either analytically or numerically and the authors recommend taking it into account when necessary. However, this procedure is very tedious and a real situation can only be approximated by calculations. Therefore, it is much easier to move the sample as close as possible to the axis of the second-order gradiometer coil by rotating the sample rod (and hence the sample) around its long axis. According to our experiences, it is best to do this using the standard stepping transport mechanism since the sample rod can be rotated directly from outside. This way the best-$R$ fit case can be attained at each temperature. Using the servo transport mechanism, the adjustment is possible only at room temperature because the sample rod cannot be rotated from outside. However, our experiences have shown that the regression value changes little when the sample is cooled down, remaining in the $R > 0.995$ range. In the light of the proposed explanation, the insensitivity of the adjustment algorithm to the temperature can be easily understood since it is the geometry of the measuring setup that essentially matters. We note that a special option for the servo transport mechanism (RTO load-lock option) would in principle allow for the axial rotation of the sample rod (we did not have this option).

Two types of geometrical imperfection can cause the radial displacement of the sample from the rotation axis of the gradiometer coil: (1) either the sample inside the sample holder and/or (2) the sample holder itself (i.e. the straw containing the sample holder). It is easy to see that a rotation of the sample rod can move the sample towards the centre of the gradiometer coil only if both imperfections mentioned above are realized. The Pd sample supplied by Quantum Design is well centered in a fused-silica tube. Therefore, the absence of the radial-displacement error (Fig. 1) and the obtained good regression values (Fig. 4) can be readily understood.

In the case of the Heusler alloy, the centering of the sample inside the sample holder is almost impossible because of its irregular shape and smaller dimensions than the sample holder. For Heusler alloys, the scattering of the magnetic moments (1–2%) found in the literature [4–6] was comparable to ours when the same sample was repeatedly dismounted and remounted with no regard to the rotation angle of the measuring rod. Using our simple method, the absolute accuracy of the measurements can be doubled and hence variations between 0.05 and 0.1 $\mu B$ in the saturation magnetic moment of the Heusler alloys can be verified.

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References