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Separation of diamagnetic and paramagnetic anisotropy by high-field, low-temperature torque measurements

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SUMMARY

The anisotropy of magnetic susceptibility (AMS) of rocks can be composed of contributions from ferromagnetic, paramagnetic and diamagnetic minerals. However, in general the AMS of only one fraction is of interest. While there are several approaches to isolate the ferromagnetic contribution to the AMS, the separation of the diamagnetic from the paramagnetic contribution is still problematic. A new method for the separation of these two contributions based on high-field torque measurements at room and low-temperature is presented. The paramagnetic anisotropy increases at low temperature according to the Curie–Weiss law, whereas the diamagnetic contribution is temperature independent. If the paramagnetic AMS is due to perfectly oblate or prolate minerals and the ratio of the susceptibility differences at two temperatures is known, paramagnetic and diamagnetic AMS can be separated. When measuring in fields high enough to saturate the ferromagnetic phases all three contributions to the AMS can be separated. The separation of paramagnetic and diamagnetic AMS is demonstrated on natural crystals and synthetic calcite–muscovite aggregates. A high-field torque magnetometer, equipped with a cryostat for measurements at 77 K, allows sensitive measurements at two different temperatures. The sensitivity at 77 K is 3×10^{-7} J and standard-sized (palaeomagnetic) samples of 11.4 cm^3 can be measured. This new method is especially suited for the investigation of diamagnetic fabrics of impure carbonate rocks.

Key words: AMS, diamagnetic, high-field torque magnetometer, low temperature, magnetic anisotropy, paramagnetic.

1 INTRODUCTION

Since the early 1960s the anisotropy of magnetic susceptibility (AMS) of rocks is used as a measure of the preferred orientation of minerals in rocks (*cf.* Tarling & Hrouda 1993; Borradaile & Henry 1997, and references therein). The susceptibility tensor measured in low field is the sum of contributions from all minerals, which include ferromagnetic, paramagnetic and diamagnetic phases (Rochette *et al.* 1983). In most studies the magnetic anisotropy of only a certain mineral phase or magnetic fraction, for example, the paramagnetic fraction, is of interest. To separate interfering signals from other minerals, several methods have been employed. High-field methods are successfully used to separate the AMS due to ferromagnetic minerals (ferromagnetic AMS) from the AMS due to diamagnetic and paramagnetic minerals (dia-/paramagnetic AMS) (Hrouda & Jelinek 1990; Martín-Hernández & Hirt 2001). Low-field measurements at low temperature have been used in several studies to enhance the paramagnetic fraction (Ihmlé *et al.* 1989; Parés & van der Pluijm 1989), or proposed to separate the paramagnetic and ferromagnetic components to the AMS (Richter & van der Pluijm 1994). To separate all three contributions to the AMS, the magnetic susceptibility must be measured in various fields and at different temperatures, as shown by Rochette *et al.* (1983) and Rochette & Fillion (1988), who used a SHE cryogenic magnetometer.

The extraction of the diamagnetic subfabric exhibits special problems. Quartz as the most abundant diamagnetic rock-forming mineral is very weakly anisotropic (Nye 1985; Hrouda 1986), whereas calcite has a considerable anisotropy (Owens & Rutter 1978; Schmidt *et al.* 2006a). However, only few studies investigated the AMS of diamagnetic fabrics (Borradaile *et al.* 1999; de Wall *et al.* 2000; Hrouda *et al.* 2000), because small amounts of paramagnetic or ferromagnetic minerals can overwhelm the diamagnetic fabric.

In this work, we present a method to separate the diamagnetic, paramagnetic and ferrimagnetic contributions to the AMS. The method is based on a combination of high-field and low-temperature measurements on a torque magnetometer. The conditions for a precise separation are that minerals contributing to the paramagnetic AMS have a perfectly oblate or prolate intrinsic AMS and that the ferrimagnetic minerals can be saturated by the applied fields. Both the theory and examples of the separation of diamagnetic and paramagnetic AMS are presented and discussed. The method allows for the quantification of the different magnetic components to the total AMS, thus opening new opportunities to investigate diamagnetic fabrics.

2 THEORY FOR THE SEPARATION OF PARAMAGNETIC AND DIAMAGNETIC AMS

The magnetic susceptibility **k** is a symmetric second-rank tensor

$$\mathbf{k} = \begin{bmatrix} k_{11} & k_{12} & k_{13} \\ k_{21} & k_{22} & k_{23} \\ k_{31} & k_{32} & k_{33} \end{bmatrix}$$

with the eigenvalues $k_1 \geq k_2 \geq k_3$. The mean susceptibility k_M is the arithmetic average of the eigenvalues ($k_M = (k_1 + k_2 + k_3)/3$). The susceptibility tensor is represented geometrically by an ellipsoid, in which k_1, k_2 and k_3 are the lengths of the principal axes. From torque measurements only the deviatoric susceptibility tensor **l** is obtained (Jelinek 1985). Geometrically, it describes the deviation of the susceptibility ellipsoid from a sphere; it can be written

$$\mathbf{l} = \mathbf{k} - k_M \mathbf{E}, \tag{1}$$

where **E** is the unit matrix, and

$$l_{11} + l_{22} + l_{33} = 0. \tag{2}$$

The magnetic anisotropy can be described by different parameters, and in this study we use the susceptibility difference $\Delta k = k_1 - k_3$ and the U-parameter (Jelinek 1981). The U-parameter is a shape factor, similar to the T-parameter (Jelinek 1981), but based on susceptibility differences, where $U = (2k_2 - k_1 - k_3)/(k_1 - k_3)$. Therefore, a perfectly oblate shape would result in $U = 1$ and a perfectly prolate shape in $U = -1$. These parameters can be determined from torque measurements, and they are, in contrast to many other parameters, independent of the bulk susceptibility. To describe the diamagnetic AMS the signed susceptibility values were used as suggested by Hrouda (2004). This leads to an oblate AMS shape ($U = 1$) for pure calcite.

Diamagnetic susceptibility and thus, its anisotropy are independent of temperature. The paramagnetic susceptibility increases with lower temperature according to the Curie–Weiss law:

$$\chi = \frac{C}{T - \theta}, \tag{3}$$

where θ is the paramagnetic Curie temperature and C is a constant. However, it must be noted that both θ and C can be anisotropic and deviations from the Curie–Weiss law occur especially at low temperatures (Ballet & Coey 1982; Richter & van der Pluijm 1994). For this reason there is not a simple relationship between paramagnetic anisotropy and temperature.

Although the following theory is generally applicable for any type of material, it is written with special consideration of rock fabrics. Let us now consider a sample with paramagnetic and diamagnetic anisotropy only, in which the paramagnetic anisotropy is carried by one mineral fraction with uniaxial single-crystal anisotropy. The torque that acts on the sample when a magnetic field is applied is the derivation of the magnetic energy of the specimen. We assume a specimen that can only rotate about its axis x_3; axes x_1 and x_2 lie in the plane of rotation. A magnetic field H in the $x_1 - x_2$-plane which makes an angle θ with the x_1-axis produces the torque

$$T = \frac{-dE}{d\theta} = \frac{1}{2}\mu_0 V H^2[(k_{22} - k_{11})\sin 2\theta + 2k_{12}\cos 2\theta], \tag{4}$$

where V is the volume of the sample (Banerjee & Stacey 1967; Jelinek 1985). Because $k_M\mathbf{E}$ is isotropic, only the deviatoric part **l** of the tensor **k** gives rise to the energy differences; it follows:

$$T = \frac{-dE}{d\theta} = \frac{1}{2}\mu_0 V H^2[(l_{22} - l_{11})\sin 2\theta + 2l_{12}\cos 2\theta]. \tag{5}$$

If the torque T is measured as a function of angle θ at room temperature (RT) and a lower temperature (LT), the corresponding deviatoric susceptibility tensors $^{\mathrm{RT}}\mathbf{l}$ and $^{\mathrm{LT}}\mathbf{l}$ can be derived. Because we consider a mixed paramagnetic-diamagnetic sample, all variables which refer to the paramagnetic or diamagnetic content will be indexed with $_{\mathrm{para}}$ or $_{\mathrm{dia}}$, respectively, in the following. The torque measured at room temperature ($^{\mathrm{RT}}T^{\mathrm{total}}$), is a superposition of a torque due to the diamagnetic ($^{\mathrm{RT}}T^{\mathrm{dia}}$) and a torque due to the paramagnetic AMS ($^{\mathrm{RT}}T^{\mathrm{para}}$), such that:

$$^{\mathrm{RT}}T^{\mathrm{total}} = {}^{\mathrm{RT}}T^{\mathrm{dia}} + {}^{\mathrm{RT}}T^{\mathrm{para}}. \tag{6}$$

The corresponding equation at low temperature is:

$$^{\mathrm{LT}}T^{\mathrm{total}} = {}^{\mathrm{LT}}T^{\mathrm{dia}} + {}^{\mathrm{LT}}T^{\mathrm{para}}. \tag{7}$$

Since the diamagnetic AMS is constant with temperature:

$$^{\mathrm{LT}}T^{\mathrm{dia}} = {}^{\mathrm{RT}}T^{\mathrm{dia}}. \tag{8}$$

However, the relation between $^{\mathrm{LT}}\,T^{\mathrm{para}}$ and $^{\mathrm{RT}}\,T^{\mathrm{para}}$ is not straightforward. At low temperature the deviatoric part $^{\mathrm{LT}}\,l^{\mathrm{para}}$ of the susceptibility tensor generates the torque. Assumed that the eigenvectors of l^{para} do not change with temperature, we define p as the ratio of the eigenvalues $l_i^{\mathrm{para}}, i = 1, 2, 3$ of l^{para} at room temperature and low temperature:

$$p_i = \frac{^{\mathrm{LT}}l_i^{\mathrm{para}}}{^{\mathrm{RT}}l_i^{\mathrm{para}}}. \tag{9}$$

We prove now that $p_i = p_j \forall i, j$ for perfectly prolate and oblate paramagnetic minerals. For a perfectly prolate ellipsoid is $l_2^{\mathrm{para}} = l_3^{\mathrm{para}}$ by definition. It follows $p_2 = p_3$. Following eq. (2), the trace of the deviatoric susceptibility matrix at room and low temperature can be written as:

$$^{\mathrm{LT}}l_1 + {}^{\mathrm{LT}}l_2 + {}^{\mathrm{LT}}l_3 = {}^{\mathrm{LT}}l_1 + 2\,{}^{\mathrm{LT}}l_2 = 0 \Rightarrow 2\,{}^{\mathrm{LT}}l_2 = -{}^{\mathrm{LT}}l_1 \tag{10}$$

$$^{\mathrm{RT}}l_1 + {}^{\mathrm{RT}}l_2 + {}^{\mathrm{RT}}l_3 = {}^{\mathrm{RT}}l_1 + 2\,{}^{\mathrm{RT}}l_2 = 0 \Rightarrow 2\,{}^{\mathrm{RT}}l_2 = -{}^{\mathrm{RT}}l_1. \tag{11}$$

Dividing these expressions gives $p_2 = p_1$. From eq. (10) it follows that $\Delta k = l_1 - l_3 = 1.5\,l_1$ is valid at both temperatures, thus p can be expressed as the ratio of the paramagnetic susceptibility differences at room and low temperature:

$$p = \frac{\Delta^{\mathrm{LT}}k^{\mathrm{para}}}{\Delta^{\mathrm{RT}}k^{\mathrm{para}}}. \tag{12}$$

Because **l** is a symmetric tensor, it holds for all elements of the tensor l_{ij}

$$^{\mathrm{LT}}l_{ij}^{\mathrm{para}} = p \cdot {}^{\mathrm{RT}}l_{ij}^{\mathrm{para}}. \tag{13}$$

This relation is invariant to rotation and addition, which implies that eq. (13) is also valid for the sum of prolate tensors with different orientations, whereby the sum tensor may be of triaxial shape. The validity of eq. (13) can be analogously shown for oblate minerals. Referring to rocks fabrics, the invariance of eq. (13) to rotation and addition implies that p for an arbitrary assemblage of grains of a paramagnetic mineral is the same as the p-value of a single crystal of this mineral, if the single-crystal AMS shape is uniaxial. However, this is not valid if the paramagnetic fraction consists of two minerals with different p-values. We can now write the torque due to the paramagnetic AMS following eq. (5):

$$\begin{aligned} {}^{LT}T^{para} &= \frac{1}{2}\mu_0 V H^2\big[\big(p\,{}^{RT}l_{22}^{para} - p\,{}^{RT}l_{11}^{para}\big)\sin 2\theta \\ &\quad + 2p\,{}^{RT}l_{12}^{para}\cos 2\theta\big] \\ &= p\frac{1}{2}\mu_0 V H^2\big[\big({}^{RT}l_{22}^{para} - {}^{RT}l_{11}^{para}\big)\sin 2\theta \\ &\quad + 2\,{}^{RT}l_{12}^{para}\cos 2\theta\big]. \end{aligned} \tag{14}$$

This implies that the torque due to the AMS of oblate or prolate paramagnetic minerals is p times greater at low temperature:

$${}^{LT}T^{para} = p\,{}^{RT}T^{para} \tag{15}$$

Eq. (7) can be rewritten as:

$${}^{LT}T^{total} = {}^{LT}T^{dia} + p\,{}^{RT}T^{para}. \tag{16}$$

Subtraction of eq. (6) from eq. (16) gives:

$${}^{RT}T^{para} = \frac{{}^{LT}T^{total} - {}^{RT}T^{total}}{p-1} \tag{17}$$

and

$${}^{RT}T^{dia} = {}^{RT}T^{total} - {}^{RT}T^{para}. \tag{18}$$

Therefore, the torque curves that correspond to the paramagnetic and the diamagnetic AMS at room temperature can be calculated from the torque curves at room and low temperature if the AMS of the paramagnetic mineral is perfectly oblate or prolate and the value of p is known.

3 METHODOLOGY AND SAMPLES

The applicability of the theory was tested on several well defined, artificial rock samples. The high-field AMS measurements were made with the torque magnetometer at the Laboratory of Natural Magnetism (LNM) at the ETH Zurich, which is routinely used for the separation of the ferrimagnetic AMS from the dia/paramagnetic and antiferromagnetic AMS (Martín-Hernández & Hirt 2001, 2004). Bergmüller *et al.* (1994) reported on a method to measure torque at 77 K with an earlier version of a cryostat, however, no practical measurements were made with this apparatus. A new cryostat was designed and built consisting of a cylindrical Dewar (Pyrex, double-walled, silver-coated) with an inner diameter of 4 cm. Standard-size samples used for palaeomagnetic studies (cylinder of 2.54 cm diameter and 2.3 cm length) can rotate freely inside the cryostat. During the entire measurement the sample is immersed in liquid nitrogen, which ensures a stable temperature throughout the volume of the sample. Disturbances by agitation due to boiling off of liquid nitrogen are not significant, as lateral movements of the sample are not recorded by the torque sensor. The program which controls the measurements was modified so that the measurement time could be reduced to about one third. The measurement time for a single plane in four fields using a rotation increment of 30° is 20 min, so that the total measurement time for a sample in three planes at two temperatures is 2 h. For weak samples the holder signal must be measured separately and subtracted from the torque curves. Compared to the precision of the instrument of 5×10^{-8} J described in Bergmüller *et al.* (1994), the sensitivity in this fast measurement mode is decreased to 3×10^{-7} J, which is equivalent to a susceptibility difference of about 3×10^{-8} SI for a standard-sized sample. During operation with the cryostat the highest field achieved is 1.5 T, which is high enough to saturate the most common ferrimagnetic minerals, such as magnetite, maghemite, phyrrhotite and greigite. By measuring in several high fields the field-invariant ferrimagnetic AMS can be subtracted from the total AMS at room and low temperature. If haematite is present in the sample and makes a significant contribution to the torque signal, it can be separated from the dia-/paramagnetic signal using the method outlined in Martín-Hernández & Hirt (2004). The remaining AMS tensors due to paramagnetic and diamagnetic minerals are then used to separate the two anisotropies according to the presented theory. Low-field AMS was measured at room temperature with a KLY-2 susceptibility meter (AGICO, Brno) in an alternating field of 300 A m^{-1} and 920 Hz.

In order to test the method to separate the diamagnetic from the paramagnetic AMS several crystal and rock samples were measured at room temperature and 77 K in four fields between 900 and 1500 mT. Table 1 provides a sample description for the three natural carbonate single crystals, two muscovite samples, test sample CMT and two synthetic calcite–muscovite aggregates. All investigated minerals have a near perfectly oblate or prolate AMS. The single crystals include calcite (C5A), dolomite (D1A), muscovite (Mu72) and siderite (S5AA) with known iron content determined by Laser Ablation ICP-MS (*cf.* Schmidt *et al.* 2006a). S24 is an aggregate of muscovite powder with a strong lattice preferred orientation. Sample CMT has a volume of 2.4 cm^3 and is composed of a diamagnetic calcite single crystal glued to paramagnetic muscovite crystals of the same composition as Mu72. Both minerals have near perfectly oblate intrinsic anisotropies with the minimum susceptibility along their respective crystallographic c-axes. The c-axis orientation of the calcite crystal in sample coordinates was determined to be 308° declination and 26° inclination. The two fractions had the high-field AMS measured individually before they were glued together; hence, the paramagnetic and the diamagnetic AMS were known. The synthetic marbles were made from calcite and muscovite powders of different proportions that were uniaxially pressed at 200 MPa along the sample cylinder axis. This created a mineral

Table 1. Sample description and iron content determined by Laser Ablation ICP-MS (Schmidt *et al.* 2006a).

Name	Description	Iron content (ppm)	Low-field susceptibility
C5A	Calcite single crystal	21	-4.1×10^{-9} m^3 kg^{-1}
D1A	Dolomite single crystal	1290	-1.2×10^{-9} m^3 kg^{-1}
S5AA	Siderite single crystal	382 700	1.2×10^{-6} m^3 kg^{-1}
Mu72	Muscovite single crystal	10 000	3.1×10^{-8} m^3 kg^{-1}
S24	Pure muscovite aggregate	12 000	3.6×10^{-8} m^3 kg^{-1}
CMT	Consists of a muscovite (0.593 g) and a calcite (5.937g) single crystal	Calcite: 26, Muscovite: 10 000	Calcite: -3.8×10^{-9} m^3 kg^{-1} Muscovite: 3.1×10^{-8} m^3 kg^{-1}
5-200-R	Aggregate of 95 per cent calcite and 5 per cent muscovite powder		-1.1×10^{-9} m^3 kg^{-1}
50-200-S	Aggregate of 50 per cent calcite and 50 per cent muscovite powder		3.7×10^{-8} m^3 kg^{-1}

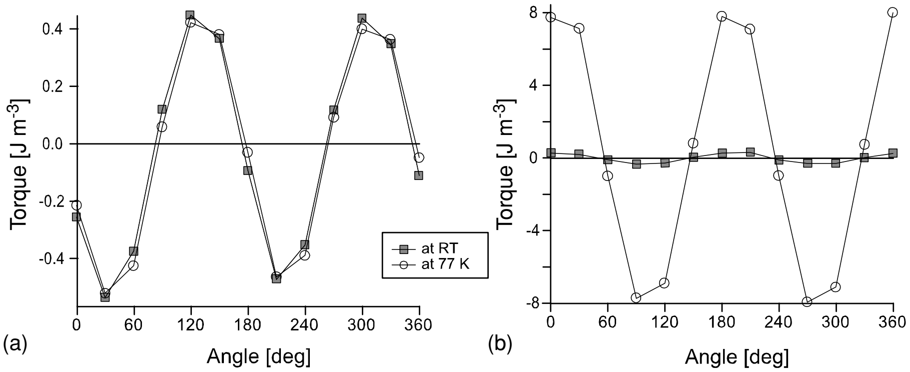

Figure 1. Torque curves at room temperature (RT) and at 77 K of (a) calcite, C5A and (b) dolomite, D1A.

Table 2. AMS of single crystals and pure muscovite aggregates at room temperature (RT) and 77 K. l_i are the principal deviatoric susceptibilities, Decl_i and Incl_i are the corresponding declinations an inclinations. Δk is the susceptibility difference $k_1 - k_3$, U is the AMS shape factor (Jelinek 1981), p is the ratio of Δk at 77 K and room temperature.

Sample	Temperature	l_1 [10^{-6} SI]	Decl_1	Incl_1	l_2 [10^{-6} SI]	Decl_2	Incl_2	l_3 [10^{-6} SI]	Decl_3	Incl_3	Δk [10^{-6} SI]	U	p
C5A	RT and 77K												1.0
D1A	RT	1.14	55	47	−0.55	156	11	−0.59	256	41	1.73	−0.95	24.3
	77K	27.5	54	46	−12.9	316	8	−14.6	218	43	42.1	−0.92	
S5AA	RT	1390	4	66	−686	254	8	−700	161	22	2090	−0.99	7.1
	77 K	9850	3	67	−4880	223	18	−4960	129	14	14810	−0.99	
Mu72	RT and 77 K												9.1
S24	RT	91.9	336	1	91.9	67	1	85.4	179	89	6.5	1.00	8.2
	77 K	107.5	328	1	107.4	57	1	54.2	183	89	53.3	1.00	

fabric in which the *c*-axes of muscovite and calcite show a preferred orientation along the cylinder axis of the samples, which results in an oblate AMS with the minimum axis at an inclination close to 90° (Schmidt *et al.* 2006b). The muscovite in samples 5-200-R and 50-200-S has the same properties as Mu72 and S24, respectively.

It is important to be aware of the different usage of the term 'paramagnetic'. In rock magnetism, minerals such as phyllosilicates and siderite are commonly termed 'paramagnetic', although they also possess a diamagnetic moment. Minerals such as calcite and muscovite are diamagnetic for their ideal chemical compositions, but often have a net paramagnetism due to substitution of iron. The *p*-value of a mineral is calculated from the susceptibility arising from the paramagnetic and the diamagnetic moments; it will vary with iron content, because the increase in anisotropy at low temperature is due to the paramagnetic content of the mineral only. However, if one aims at the separation of the contribution of muscovite to the AMS, the entire mineral is regarded as the 'paramagnetic fraction' and the *p*-value for muscovite must be chosen for the separation. In this study the diamagnetic AMS of muscovite is considered together with the paramagnetic component, therefore, muscovite will be regarded as the paramagnetic component throughout this paper.

4 RESULTS

4.1 Crystals/single-phase samples

Single crystals and single-phase samples were measured to determine the *p*-factor for individual minerals. Note that these *p*-values for the paramagnetic minerals will include their diamagnetic contribution. The calcite crystal C5A is very pure with only 21 ppm Fe, and it has a diamagnetic susceptibility of pure calcite (Schmidt *et al.* 2006a). The high-field AMS of C5A was the same at room and low temperature (Fig. 1a, Table 2). Its AMS is purely diamagnetic and independent of temperature. The dolomite crystal, D1A, contains 1290 ppm Fe, but its low-field susceptibility is still negative at room temperature. Shape and orientation of the AMS ellipsoids were identical at both temperatures; Δk at 77 K was 24.3 times greater than at room temperature (Fig. 1b). The siderite crystal contains 382 700 ppm Fe compared to 2500 ppm Ca and is paramagnetic. It showed a perfectly prolate AMS at 77 K (Table 2). The orientation of the principal axes was the same as at room temperature, but Δk was 7.1 times greater. The muscovite crystal Mu72 contains 10 000 ppm iron and its bulk susceptibility is 3.1×10^{-8} m^3 kg^{-1}. It was measured only in one plane normal to the basal plane. p was determined to be 9.1. The pure muscovite sample S24 contains 12 000 ppm Fe and its bulk susceptibility is 3.6×10^{-8} m^3 kg^{-1}. The AMS is perfectly oblate and the ratio of Δk at room temperature and 77 K is 8.2. These values for p from the muscovite samples were then used for the separation of the composite samples.

4.2 CMT

Measurements of the individual components of sample CMT show a purely oblate diamagnetic AMS for the calcite single crystal and a less oblate AMS of the muscovite fraction ($U = 0.73$). For the separation of the diamagnetic and paramagnetic AMS from low- and room-temperature measurements a p-factor of 9.1 was used. In Table 3, the values of the anisotropy from measurements of the individual parts are shown together with the values obtained by the separation. The contributions of calcite and muscovite to the AMS of CMT are of the same order. The separated directions of the minimum axes, which correspond to the *c*-axes, are very close to the actual values (Fig. 2a). Also the maximum and intermediate directions of the slightly non-oblate paramagnetic fraction are close

Table 3. Eigenvalues (l_i), declinations (Decl$_i$) and inclinations (Incl$_i$) for the deviatoric susceptibility tensors of the calcite–muscovite samples at room temperature; 'dia', 'para' and 'ferro' refer to diamagnetic, paramagnetic and ferromagnetic contributions to the AMS; all values are measured in high fields unless indicated. 'individual' are values from measurements of the individual contributions, 'separated' are values obtained from the separation.

Sample	Component	Method	l_1[10^{-6} SI]	Decl$_1$	Incl$_1$	l_2[10^{-6} SI]	Decl$_2$	Incl$_2$	l_3[10^{-6} SI]	Decl$_3$	Incl$_3$	Δk [10^{-6} SI]	U
CMT	dia+para+ferro	Low-field	0.55	154	84	0.38	20	4	−0.93	290	5	1.48	0.77
	dia	Individual	0.35			0.35			−0.69	308	26	1.04	1.00
		Separated	0.37	217	1	0.30	126	55	−0.68	308	35	1.05	0.86
	para	Individual	0.41	356	49	0.26	178	41	−0.67	87	1	1.08	0.73
		Separated	0.54	355	67	0.24	179	23	−0.78	88	1	1.33	0.55
5-200-R	dia+para+ferro	Low-field	0.66	6	16	0.04	273	8	−0.69	157	72	1.35	0.08
	dia+para	High-field	0.18	261	1	0.17	351	4	−0.34	152	86	0.54	0.97
	dia	Separated	0.12	272	2	0.12	2	3	−0.24	152	86	0.36	0.95
	para	Separated	0.06	332	2	0.05	62	2	−0.11	195	87	0.17	0.90
50-200-S	dia+para+ferro	Low-field	2.44	87	3	2.08	177	1	−4.53	283	87	6.97	0.90
	dia+para	High-field	1.45	65	0	1.39	155	2	−2.84	333	88	4.30	0.97
	dia	Separated	0.02	237	34	−0.01	55	56	−0.01	146	1	0.03	−0.81
	para	Separated	1.44	73	0	1.41	163	2	−2.85	326	88	4.29	0.98

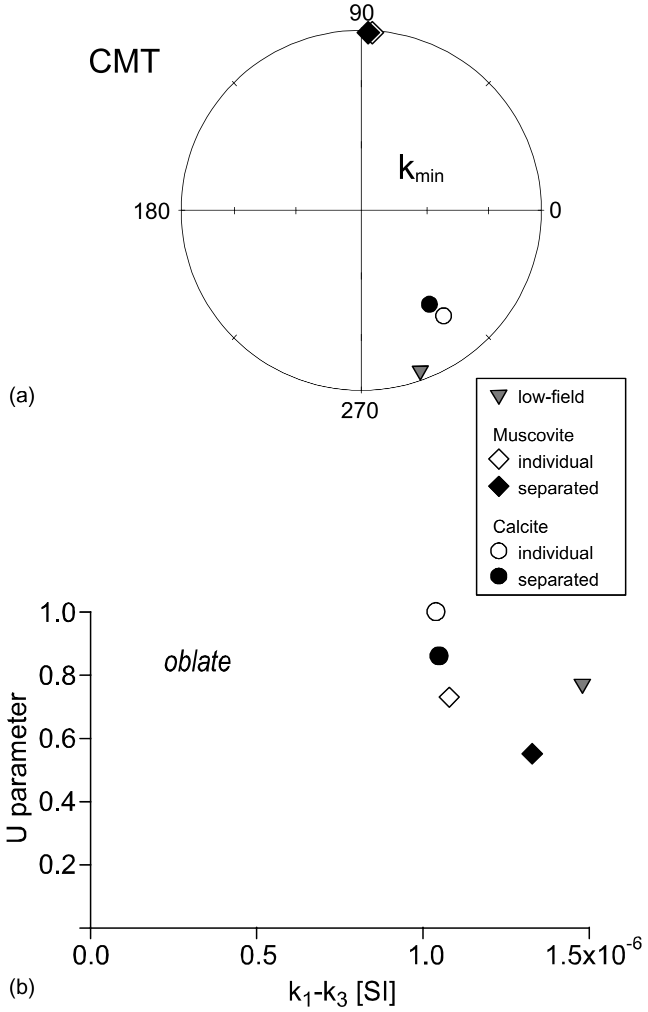

Figure 2. AMS of CMT from low-field measurement, high-field measurements of individual components and values obtained by the separation for the diamagnetic (calcite) and paramagnetic (muscovite) fraction of sample CMT, (a) directions of minimum susceptibility axes and (b) modified Jelinek plot.

to the expected values. The difference in the eigenvalues is 10 per cent on average. The U-parameters are close to the values of the individual measurements, but the shapes tend to be more triaxial (Fig. 2b). The results from low-field measurements are close to the sum of the paramagnetic and diamagnetic AMS from high-field measurements, which indicates that no significant ferromagnetic contribution to the AMS is present.

4.3 Synthetic marbles

The measurements of the synthetic marbles provide a test how the diamagnetic AMS can be separated in the presence of a small and a large paramagnetic component. The low-field AMS is higher than the sum of the paramagnetic and diamagnetic AMS due to a ferromagnetic component which was separated in high fields. In the sample 5-200-R the paramagnetic and the diamagnetic contributions are of the same order and show an oblate AMS with the inclination of the minimum axis close to 90° (Table 3). Both contributions were properly separated. In sample 50-200-S with 50 per cent muscovite the paramagnetic AMS is oblate and much stronger due to the higher muscovite content. The diamagnetic contribution is a small percentage of the total AMS; its more triaxial to prolate shape does not reflect the c-axis concentration at high inclinations. This implies that in sample 50-200-S the diamagnetic component is overwhelmed by the paramagnetic AMS and cannot be properly separated.

5 DISCUSSION

5.1 Applicability of the theory to rocks

The method to separate out the diamagnetic AMS is based on several assumptions which may not be fulfilled for all rocks. Firstly, all minerals that carry the paramagnetic anisotropy must have the same p-value. This is the case is most rocks, as the paramagnetic AMS is often carried by only one mineral. A second assumption is that the deviatoric tensor of the AMS of the paramagnetic minerals at low temperature corresponds to the tensor at room temperature scaled by a factor, that is, the principal directions and the shape are the same. However, it cannot be excluded that this may not be the case for certain minerals, for example, if they exhibit a crystallographic transition or undergo magnetic ordering at low temperature. Changes in mineral magnetism at low temperatures are not extensively investigated, especially when applying high fields. Thirdly, the pre-condition of the oblateness or prolateness of the paramagnetic minerals is met by the most common anisotropic minerals such as phyllosilicates and siderite. The application of the method to triaxial minerals is not known, but may still yield useful results. Fourthly, the theory assumes that the measured torque is only due to diamagnetic and paramagnetic contributions. In practice the AMS of only few lithologies is not influenced by ferromagnetic minerals. In the presented method the torque due to ferrimagnetic minerals was separated by measurements in high fields. The AMS due to haematite can be separated using the method by Martín-Hernández & Hirt (2004), but the influence of other antiferromagnetic minerals like goethite has to be excluded. Note that at 77 K magnetite is below the Verwey transition and its magnetic properties are different.

5.2 AMS of titanomagnetite below the Verwey transition

The separation of the ferromagnetic AMS in high fields assumes that the torque due to ferromagnetic minerals is constant with field. At room temperature this is valid for the most common ferromagnetic phases, (titano)magnetites, when the applied field is higher than the saturation field of about 300 mT. It is an open question whether these phases are also saturated at 77 K, because the magnetic properties of magnetite are fundamentally different when it is cooled through the Verwey transition at about 120 K. Therefore, we have to estimate the effects of crystalline and shape anisotropy at low temperature.

The magnetocrystalline anisotropy of magnetite below the Verwey temperature T_V becomes much larger in amplitude (Li 1932; Bickford 1953) and changes from cubic to monoclinic (Yoshida & Iida 1977). This results in a strong 2θ-component in torque curves for single crystals on the order of 2.5×10^5 J m^{-3} in the plane containing the monoclinic *a*-axis as shown by Abe *et al.* (1976). The dependence of torque with applied field at 77 K has not been investigated in this study. However, a preferred orientation of the monoclinic axes is only generated when magnetite is cooled through T_V in a field (Williams & Bozorth 1953; Palmer 1963). When it is cooled in zero-field, the axes are randomly distributed and the torque curve is dominated by a 4θ-signal (Pearson & Cooper 1961; Höhne *et al.* 2000). Therefore, we do not expect a 2θ-component due to ferromagnetic magnetocrystalline anisotropy in zero-field cooled rock samples.

The shape anisotropy is linear to the square of the magnetization and is constant in fields above saturation. Below T_V the induced magnetization is on the order of the room-temperature values (Weiss & Forrer 1929; Domenicali 1950), but the field needed to reach saturation in magnetite was shown to increase up to 2 T because of a paraprocess (Belov 1994; Muxworthy & McClelland 2000). Özdemir & Dunlop (1999) reported that saturation is reached along the cubic [001] axis at about 0.2 T at 10 K. According to Kakol *et al.* 1991 magnetite with low titanium content reached saturation at 77 K at about 400 mT; higher titanium content shifted saturation towards higher fields. However, in the lowest field of 900 mT applied in this study magnetite is saturated to more than 95 per cent. The possible increase of magnetization in higher fields is very small, so that we can regard our samples as saturated. Problems could only arise in samples, in which the shape anisotropy dominates the torque signal at high fields. To avoid problems with unsaturated titanomagnetites, measurements could be made at dry ice temperature (195 K) above the Verwey transition. In summary, the occurrence of a 2θ torque signal at 77 K due to titanomagnetite, which increases with field, cannot be generally excluded, but is expected to negligible in most samples. Rock samples should be zero-field cooled before the measurement to avoid a crystallographic preferred orientation of the monoclinic phase. Torque curves that show distortion or a non-linear increase of the torque against field square should be discarded.

5.3 Discussion of results

The differences between the principal susceptibilities of all investigated paramagnetic single crystals increase at low temperature; the anisotropy shape and the orientation of the principal axes remain the same. The deviatoric tensor at low temperature can be considered to be the deviatoric tensor at room temperature multiplied by p. The values for p determined from the crystals are only valid for minerals with the same chemical composition. Variations in iron content, which are common for calcite and muscovite, may lead to variations in p. The extremely high value of p of the dolomite sample can be explained by interference of the diamagnetic oblate AMS of the carbonate matrix and the prolate AMS of substituted iron (Schmidt *et al.* 2006a). The susceptibility difference at room temperature $\Delta^{\mathrm{RT}}k$ (*cf.* the denominator in eq. 12) is small, because the oblate and the prolate anisotropies are approximately equal and, therefore, self-cancelling. At low temperature the paramagnetic susceptibility difference is enhanced which results in a high value for p.

The anisotropies of muscovite and calcite in sample CMT were successfully separated in amplitude and direction. Repeated measurements showed random variations in both quantities for the diamagnetic and paramagnetic part; that is, the better agreement of the values of Δk for calcite compared to muscovite is not systematic. However, the anisotropy shapes tend systematically towards more triaxial values; this suggests that measurement uncertainties smooth the AMS ellipsoid. These results show that the separation of very weak anisotropies is possible with quite high precision.

The results from samples 5-200-R and 50-200-S show a good separation of the AMS in carbonate rocks with low phyllosilicate content, whereas the result is unsatisfactory at high phyllosilicate content. In sample 50-200-S the paramagnetic signal at 77 K is about 20 times stronger than the diamagnetic signal. This makes a proper separation impossible. Although sample 50-200-S contains 10 times more muscovite than sample 5-200-R, its paramagnetic AMS is more than 10 times stronger. This indicates the better alignment of the phyllosilicates in sample 50-200-S.

5.4 Influences on the quality of the separation

The quality of the separation is determined by the following.

(i) The sensitivity of the instrument.
(ii) The precision of sample orientation.
(iii) The choice of the value for p.

Fig. 3 illustrates the precision of the measurements. The torque curves at high and low temperature and the ratio of the values for the siderite crystal S5AA are shown. The torque at 77 K should be 7.1 times the value at room temperature for all positions, however, we find values between 6.5 and 7.5. These deviations result from imperfect orientation and measurement uncertainties. If there are slight misorientations of the sample between measurement at room and low temperature, phase shifts between the torque curves occur. Shifts of only 1° can result in considerable errors. Therefore, a positioning accuracy in the order of 0.2° is advisable. The choice of the correct value for p is important; however, if the paramagnetic signal

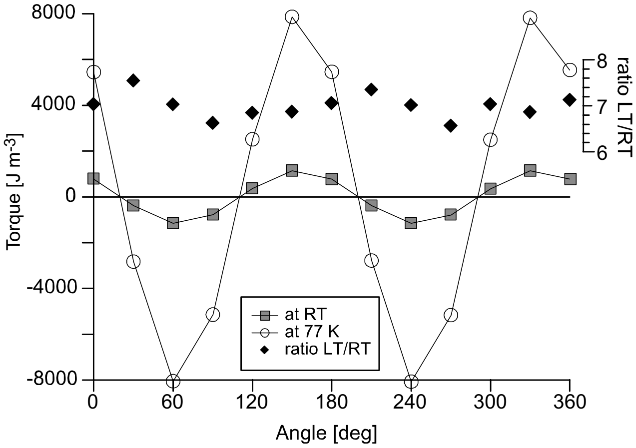

Figure 3. Torque curves of the siderite S5AA at room temperature (RT) and at 77 K (LT). The ratio of the values at low and high temperature is indicated for every angle.

does not dominate, the result is not very sensitive to variations in *p*. Deviations of 10 per cent from the correct value will result in a deviation of about 10 per cent in the eigenvalues.

5.5 Determination of the value of *p*

The most precise way to determine *p* is the direct measurement of the AMS of the paramagnetic fraction at both temperatures. This was done with the composite sample CMT and made a successful separation possible. For natural samples *p* can be determined in a similar way if the paramagnetic fraction can be extracted from the rock sample, for example, by dissolution of the carbonate minerals. If a direct measurement is not possible, *p* could be inferred from data in the literature provided that the paramagnetic mineral, which carries the anisotropy, is known. However, this requires measurements:

(i) In high fields to eliminate any contribution from ferromagnetic inclusions.
(ii) Along the principal axes of susceptibility.
(iii) At room temperature and at low temperature.

Furthermore, the Fe^{2+} content in the mineral should be known (e.g. Ballet & Coey 1982; Beausoleil *et al.* 1983; Rochette 1988; Richter & van der Pluijm 1994). Ballet & Coey (1982) investigated several phyllosilicates and associated the AMS with various amounts of ferrous iron. Values for *p* calculated from their data give 7.7 for muscovite, 7.8 and 18.2 for two different samples of biotite, and 6.7 and 13.7 for two samples of vermiculite. This wide range of values shows, that care must be taken if the chemical composition of the paramagnetic minerals is not known. However, small deviations of less than 1 from the true value still give a good separation.

6 CONCLUSIONS

A theory of the separation of diamagnetic and paramagnetic AMS of rocks by means of high-field torque measurements at room temperature and low temperature has been presented. The theory presumes that the paramagnetic minerals have a perfectly oblate or prolate AMS with coinciding principal directions at low and room temperature, and that the ratio of the AMS of the paramagnetic fraction at room temperature and low temperature is known. For practical realization a torque magnetometer was modified to allow for fast and sensitive measurements of standard-sized rock samples at 77 K. Tests of the method on single crystals and several two-phase samples proved the applicability of the theory. Together with the capability of the instrument to separate the ferromagnetic AMS it is possible to determine diamagnetic, paramagnetic and ferromagnetic contributions to the AMS separately. The applicability of the method to different lithologies needs to be investigated in further studies. Problems could arise if different paramagnetic minerals contribute to the AMS or unsaturated ferromagnetic phases occur.

The presented method is especially suited to measure diamagnetic subfabrics of micaceous carbonate rocks, which record early phases of deformation or primary sedimentary fabric prior to dolomitization. It is also capable of discriminating between the diamagnetic AMS of the carbonate matrix and the paramagnetic AMS due to substituted iron in calcite. Torque measurements at low temperature could also be used to increase weak paramagnetic AMS and to investigate the magnetocrystalline anisotropy of magnetite below the Verwey transition.

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