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Published version:

DOI:10.1002/2015JB012255

Lanci, L.; Zanella, E.. The anisotropy of magnetic susceptibility of uniaxial superparamagnetic particles: Consequences for its interpretation in magnetite and maghemite bearing rocks. JOURNAL OF GEOPHYSICAL RESEARCH. None pp: 1-11.

DOI: 10.1002/2015JB012255

The anisotropy of magnetic susceptibility of uniaxial superparamagnetic particles: Consequences for its interpretation in magnetite and maghemite bearing rocks

Luca Lanci[1] and Elena Zanella[2]

Corresponding author: L. Lanci, Department of Pure and Applied Science, University of Urbino, Via S. Chiara 27, I-61029, Urbino (PU), Italy. (luca.lanci@uniurb.it)

[1]Department of Pure and Applied Science,

University of Urbino, Urbino (PU), Italy

[2]Department of Earth Sciences,

University of Turin (TO), Turin Italy.

Abstract. A simple model that provides a quantitative description of the magnetic susceptibility of superparamagnetic to stable single-domain uniaxial magnetic particles can be built in the framework of the theory of stochastic resonance. This model expands that of *Mullins and Tile* [1973] for superparamagnetic grains by considering the dependence of superparamagnetic susceptibility on the particle orientation and thus describes the anisotropy of magnetic susceptibility (AMS) of ensembles of superparamagnetic as well as single-domain particles. The theory predicts that, on the contrary of stable single-domain, the maximum anisotropy of superparamagnetic particles is parallel to their easy axis and shows that the AMS of ensembles of uniaxial particle is strongly dependent on the distribution of particle grain-size, coercivity, measurement temperature and frequency. It also explains why the inverse AMS pattern expected for stable single-domain particles is rarely observed in natural samples. We use examples of well-characterized obsidian specimens to show that, as predicted by the theory, in the presence of significant superparamagnetic contributions the maximum susceptibility axis of AMS is directed along the preferential direction of particles easy axis.

1. Introduction

Fine-grained magnetic particles are very common in nature and their anisotropy of magnetic susceptibility (AMS) has been commonly used in a variety of environmental and tectonic studies [e.g., *Rochette et al.*, 1992]. In these magnetic particles of nanometric size, the transition from stable single-domain to superparamagnetic state is marked, among other effects, by a severalfold increase of magnetic susceptibility. This transition occurs in a relatively narrow interval of temperature and volumes when the particle relaxation time becomes comparable to the measurement time or, if measurements are made in alternating field, to about the half-period. Their presence can be quantified with susceptibility measurements at different temperatures or frequencies, which are often employed in environmental studies on sediments and soils. However, despite the interest in AMS and in superparamagnetic grain, the AMS of superparamagnetic grain is not well studied.

Neglecting the effect of temperature, the orientation of magnetic moment in uniaxial single-domain particles is determined by the local minima of the particle self-energy and an induced magnetization, hence their susceptibility, results from the shift of such minima in an applied field [*Stoner and Wohlfarth*, 1948]. When the probability of energy barrier hopping caused by thermal fluctuations becomes significant, the susceptibility is increased by a superparamagnetic term that adds to the stable single-domain susceptibility. The superparamagnetic susceptibility of an ensemble of non-interacting particles can be described as that of a paramagnetic gas only if the particles blocking energy is negligible compared to thermal energy. A more complete model for an ensemble of particles with easy-axis parallel to the magnetizing field, was proposed by *Mullins and Tile*

[1973], based on *Néel* [1949] theory. This model explains phenomena occurring during the superparamagnetic-stable single-domain transition such as the quadrature susceptibility (i.e., the susceptibility due to the component of magnetization 90° out of phase from the driving field) and frequency dependence. In the rock- and paleo-magnetic literature, the latter was discussed in detail by *Worm* [1998] while *Shcherbakov and Fabian* [2005] and *Egli* [2009] investigated inverse methods to compute magnetic grain-size distributions using the frequency-dependent susceptibility measured at different temperatures.

Although the *Mullins and Tile* [1973] model is still the main reference within the rock- and paleo-magnetic scientific community, a vast amount of work on AC susceptibility is available in the physics literature. The theory of stochastic resonance has been applied to the AC susceptibility to describe interwell hopping both in the case of uniaxial and triaxial particles [e.g., *Coffey et al.*, 2001; *Raikher et al.*, 2003; *Kalmykov et al.*, 2005, and references therein]. The effect of intrawell contribution was introduced by *Svedlindh et al.* [1997] and a semi-analytical expressions for the in-phase and quadrature susceptibility that include the effect of surface anisotropy and (weak) dipolar interactions in the limit of small field was developed by *Vernay et al.* [2014]. Many of these models attempt to solve the most general problem based on the theory of *Brown* [1963], considering simultaneously both interwell and intrawell fluctuations over a wide range of controlling parameters. This generally involves solving the Fokker-Plank equation with a periodically varying potential and leads to complicated calculations that can be evaluated only using a numerical approach. Moreover most calculations contemplate only the case of particles with anisotropy axis parallel to the field direction.

This paper presents a model describing the superparamagnetic susceptibility (χ_{SP}) of uniaxial particles from the point of view of the theory of stochastic resonance [e.g., *McNamara and Wiesenfeld*, 1989; *Gammaitoni et al.*, 1998]. The proposed model is simplified by restricting to the case of low-field susceptibility measured at AC frequencies satisfying the adiabatic assumption. Within these limitations, which comprise virtually all kind of rock-magnetic measurements, it is possible to consider a straightforward, bi-state model that captures an accurate representation of uniaxial magnetic particles and yield simple analytical expressions. It is shown that the χ_{SP} derived from this model is equivalent to that of *Mullins and Tile* [1973] for particles with easy axis parallel to the field, hence it is supported by the experimental evidence available in the literature. The proposed model, however, expands the previous one introducing the dependence of χ_{SP} on particle orientation and combining the interwell (superparamagnetic) and the intrawell (ferrimagnetic) susceptibility. We focus on this aspect in order to quantify the AMS contribution of superparamagnetic and stable single-domain grains showing that superparamagnetic susceptibility is very likely to dominate the AMS pattern in many natural rock samples. Experimental measurements from obsidians are shown to support the theory and the consequence on AMS measurements in rock-magnetism are discussed.

2. Theory

2.1. Stochastic Resonance of Bi-state Magnetic Particles

In ferromagnetic (*s.l.*) material the magnetic susceptibility χ is defined as $\chi = \frac{\partial M}{\partial H}$ at $H = 0$ [e.g., *Bertotti*, 1998]. Let's consider the magnetic susceptibility χ_{SP} due to the barrier hopping caused by thermal fluctuation in a uniaxial particle of volume v, whose geometry is depicted in Fig. 1a, subject to an alternating field with intensity H and angular frequency ω. In zero field, the minima of the particle potential energy E are symmetrical and separated by the potential barrier $E_b = K_u v$, where K_u is the anisotropy constant. Thermally-induced hopping between the potential wells occurs but in this condition the symmetry of the system enforces the average effect to vanish. In the presence of a periodic field H, the double-well potential E is tilted back and forth, thereby raising and lowering successively the potential barriers of the right and the left well, respectively, in an antisymmetric manner (Fig. 1b). The periodic forcing due to the alternating field is too weak to let the magnetic moment move periodically from one potential well into the other one, however it introduces an asymmetry in the system and lets the stochastic interwell hopping come into play. Statistical effects of the thermal switching becomes particularly relevant when the average waiting time between two thermally-induced interwell transitions is comparable with the half-period of the alternating field, causing an increase of the interwell hopping frequency. This phenomenon is called stochastic resonance.

The theory presented in this paper assumes a small driving AC field H (ideally $H \rightarrow 0$ for the initial susceptibility) and a field frequencies $\omega \ll f_0$ where f_0 is the atomic attempt frequency, with $f_0 \approx 1$ GHz when computed from Néel's relaxation times [*Moskowitz et al.*, 1997]. These assumptions are fulfilled by rock-magnetic measurements at room-temperature and low-temperature. The discrete two-states model implies that the distribution of the moment orientation is sharply peaked at the minima of the potential energy, which is a reasonable assumption for $\frac{K_u v}{k_B T} \geq 5$, hence for magnetic particles with a spherical equivalent diameter larger than a few nanometers [e.g., *García-Palacios*, 2000]. In extremely small particles, however, quantum fluctuations become relevant and set a more stringent limit to the validity of models based on classical mechanic. Although this limit is not precisely defined, it has been suggested [*Jones and Srivastava*, 1989] that a number of atoms $< 10^3$, which roughly corresponds to about 5 nm diameter, are the smallest particles that can be studied with classic models.

Within the above limits, this theory provides a useful model to calculate the average magnetization caused by thermally-induced interwell hopping of uniaxial particles subject to an alternating magnetic field, hence their AC superparamagnetic susceptibility.

2.2. Superparamagnetic Susceptibility

In the bi-state system considered above, the magnetic moment can be found in the states (potential minima) $\pm$ with a probability ($n_\pm$) given by the master equation:

$$\frac{dn_+(t)}{dt} = -n_+(t)\,W_+ + n_-(t)\,W_-, \tag{1}$$

which is equivalent to that commonly used for deriving Néel relaxation time except that here the transition rate $W_\pm(t)$ out of the $\pm$ state, is periodically modulated. The solution to this first-order differential equation (1) was given by *McNamara and Wiesenfeld* [1989]

$$\begin{aligned} n_+(t) =&\ g^{-1}(t)\left(n_+(t_0)\,g(t_0) + \int_{t_0}^{t} W_-(t')\,g(t')d(t')\right) \\ g(t) =&\ \exp\left(\int^{t} (W_+(t') + W_-(t'))\,dt'\right) \end{aligned} \tag{2}$$

who proposed to use a periodically modulated escape rate $W_\pm$ of the type

$$W_\pm(t) = f(\mu \pm \eta_0 cos(\omega t)) \tag{3}$$

where μ in a dimensionless ratio between potential barrier and thermal noise of the unperturbed system, and η_0 is the amplitude of the periodical modulation.

In a uniaxial magnetic particle the escape rate function $f(t)$ is proportional to an exponential function [e.g., *Néel*, 1949], the energy barrier of the unperturbed particle is

$\mu = -K_u v/k_B T$ and periodical fluctuation $\eta_0 = -E_H/k_B T$ is given by the ratio between the Zeeman energy and the thermal noise. Following *McNamara and Wiesenfeld* [1989], eq. (3) can be expanded in a Taylor series for small $\eta_0 cos(\omega t)$ and after substituting μ and η_0 we obtain,

$$W_{\pm}(t) = C\, e^{-\frac{K_u v}{k_B T}} \left(1 \mp \frac{E_h}{k_B T}\cos(\omega t) + \frac{1}{2}\left(\frac{E_h}{k_B T}\right)^2 \cos^2(\omega t) \mp \frac{1}{6}\left(\frac{E_h}{k_B T}\right)^3 \cos^3(\omega t)^3 + \cdots\right), \tag{4}$$

hence

$$W_+(t) + W_-(t) = 2C\, e^{-\frac{K_u v}{k_B T}} \left(1 + \frac{1}{2}\left(\frac{E_h}{k_B T}\right)^2 \cos^2(\omega t) + \cdots\right), \tag{5}$$

where C is a proportionality factor taken such that $2C$ corresponds to the Néel pre-exponential factor f_0, hence $2C\, e^{-\frac{K_u v}{k_B T}} = 1/\tau$ is the inverse of Nèel's relaxation time.

The integral (1) can now be performed analytically to the first order in $\eta_0 = -E_H/k_B T$ [e.g., *McNamara and Wiesenfeld*, 1989; *Gammaitoni et al.*, 1998],

$$n_+(t|x_0, t_0) = \frac{1}{2}\left(e^{-\frac{1}{\tau}(t-t_0)}\ (\delta_{x_0} - 1 - \kappa(t_0)) + 1 + \kappa(t)\right) \tag{6}$$

where $\kappa(t) = 1/\tau\, \frac{E_h}{k_B T}\cos(\omega t - \Phi)/\sqrt{1/\tau^2 + \omega^2}$ and $\Phi = \arctan(\omega\, \tau)$. According to *McNamara and Wiesenfeld* [1989] the quantity $n_+(t|x_0, t_0)$ represent the probability that the magnetic moment in the state + at time t given the initial state, and the Kronecker delta δ_{x_0} is 1 when the system initially in state +. The mean value $\langle n_+(t)\rangle$ is obtained by averaging over a sufficiently long time (ideally $t_0 \to -\infty$) so that the memory of the initial conditions gets lost obtaining,

$$\langle n_+(t)\rangle = \frac{E_h}{k_B T\, \sqrt{1 + \omega^2 \tau^2}}. \tag{7}$$

The average superparamagnetic magnetization of a particle can then be expressed as

$$M = \langle n_+\rangle\, M_s\, \cos(\phi - \theta). \tag{8}$$

where $\phi - \theta$ is the angle between the direction of the time-dependent field H and the magnetic moment M_s. For uniaxial particles in the hypothesis of small field one can find [e.g., *Lanci*, 2010]

$$M = \langle n_+ \rangle \, M_s \, \cos\left(\phi - \frac{\mu_0 \, M_s \, H \sin(\phi)}{\mu_0 \, M_s \, H \cos(\phi) + 2K_u}\right). \tag{9}$$

Moreover, in small field H, and consequently small angle θ, the Zeeman energy can be reduced to the first term of its Taylor series expansion around $\theta = 0$ leading to $E_H = \mu_0 \, M_s \, v \, H(\cos(\phi) + \sin(\phi)\theta)$. Substituting in (7) one obtains the following expression for $\langle n_+ \rangle$

$$\langle n_+ \rangle = \frac{\mu_0 \, H \, M_s \, v \, \cos(\phi)}{k_B T \sqrt{1 + \omega^2 \tau^2} - \mu_0 \, H \, M_s \, v \, \sin(\phi)}. \tag{10}$$

The variation of $\langle n_+ \rangle$ as a function of the temperature and grain orientation ϕ is shown in Fig. 2. Intuitively, the rapid initial increase of $\langle n_+ \rangle$ is due to magnetic moment unblocking, while the subsequent $\propto 1/T$ decrease can be explained by the increasing number of random interwell jumps, which cause a stronger randomization of the system.

The superparamagnetic susceptibility χ_{SP} of a grain with orientation ϕ can be calculated from the equations (9) and (10)

$$\chi_{SP}(\phi) = \frac{\partial}{\partial H} \left[\frac{\mu_0 \, H \, M_s \, v \, \cos(\phi)}{k_B T \sqrt{1 + \omega^2 \tau^2} - \mu_0 \, H \, M_s \, v \, \sin(\phi)} \, M_s \, \cos\left(\phi - \frac{\mu_0 \, M_s \, H \sin(\phi)}{\mu_0 \, M_s \, H \cos(\phi) + 2K_u}\right)\right]. \tag{11}$$

For $H \rightarrow 0$ one obtains

$$\chi_{SP}(\phi) = \frac{\mu_0 \, M_s^2 \, v \, \cos^2(\phi)}{k_B T \sqrt{1 + \omega^2 \tau^2}}. \tag{12}$$

The in-phase χ'_{SP} e quadrature χ''_{SP} components of χ_{SP} can be obtained straightaway using the phase angle $\Phi = \arctan(\omega\,\tau)$

$$\chi'_{SP}(\phi) = \frac{\mu_0\,M_s^2\,v\,\cos^2(\phi)}{k_B T\,(1+\omega^2\tau^2)} \tag{13}$$

$$\chi''_{SP}(\phi) = \frac{\mu_0\,M_s^2\,v\,\cos^2(\phi)\,\tau\,\omega}{k_B T\,(1+\omega^2\tau^2)}. \tag{14}$$

Equations 13 and 14 generalize *Mullins and Tile* [1973] introducing the dependence on particle orientation ϕ. $\chi_{SP}(\phi)$ shows a dependence on $\cos^2(\phi)$ indicating that the susceptibility of grains with easy-axis orthogonal to the field direction is null and that the largest contribution to superparamagnetic susceptibility is given by grains with easy-axis parallel to the field direction.

The in-phase χ'_{SP} e quadrature χ''_{SP} superparamagnetic susceptibility can be reduced to the isotropic case of *Mullins and Tile* [1973] by averaging them over ϕ uniformly distributed on a sphere obtaining

$$\chi'_{SP} = \frac{\mu_0\,M_s^2\,v}{3\,k_B T}\;\frac{1}{1+\omega^2\tau^2} \tag{15}$$

$$\chi''_{SP} = \frac{\mu_0\,M_s^2\,v}{3\,k_B T}\;\frac{\omega\tau}{1+\omega^2\tau^2}. \tag{16}$$

where the two factors are separated to highlight the low-field approximation of the Curie law term and the stochastic term.

The derivation of eq. (13) and eq. (14) has been criticized by one of the reviewer (A. Newell), although he admits that the result is correct. For this reason we forced ourself to adhere pedantically the original theory developed by *McNamara and Wiesenfeld* [1989] and revised by *Gammaitoni et al.* [1998] in such a way that their derivation can be easily followed by the readers.

One further criticism concern the concept of stochastic resonance, in particular neglecting that the peak shown in Fig. 2 represent the effect of stochastic resonance. Here we answer quoting *Gammaitoni et al.* [1998] who, referring to equivalent of $\langle n_+ \rangle$ (their x) write: " *...we note that the amplitude x first increases with increasing noise level, reaches a maximum, and then decreases again. This is the celebrated stochastic resonance effect.*"

2.3. Stable Single-domain and Superparamagnetic Susceptibility

In our two-state model, with the distribution of the moment orientation is sharply peaked at the potential energy minima, the intrawell contribution to magnetic susceptibility consists of the ferromagnetic (*s.l.*) susceptibility χ_F due to the shift of the self-energy minima in the applied field [e.g., *O'Reilly*, 1984; *Lanci*, 2010]. In single uniaxial particles with orientation ϕ (Fig. 1a), the initial ferromagnetic susceptibility χ_F is described by [e.g., *Lanci*, 2010]

$$\chi_F(\phi) = \frac{\mu_0 \, {M_s}^2 \, \sin^2(\phi)}{2 \, K_u}. \tag{17}$$

Coupling together the superparamagnetic in-phase χ'_{SP} and the stable single-domain susceptibility χ_F, the interwell jumps and intrawell contribution in the physics literature [e.g., *Svedlindh et al.*, 1997], the (in-phase) magnetic susceptibility per unit of volume, as generally measured by K-bridge, for an ensemble of grains with orientation ϕ can be expressed as the sum of equations (12) and (17) i.e.:

$$\chi'(\phi) = \frac{\mu_0 \, M_s^2 \, v \, \cos^2(\phi)}{k_B T \, (1 + \omega^2 \tau^2)} + \frac{\mu_0 \, {M_s}^2 \, \sin^2(\phi)}{2 \, K_u}. \tag{18}$$

In the isotropic case of an ensemble of single-domain uniaxial grains with uniformly distributed orientation on a sphere one has

$$\chi' = \frac{\mu_0 \, M_s^2 \, v}{3 \, k_B T} \, \frac{1}{1 + \omega^2 \tau^2} + \frac{\mu_0 \, M_s^2}{3 K_u} \tag{19}$$

which is equivalent to the formulation of *Shcherbakov and Fabian* [2005] and the so-called Néel model of *Egli* [2009].

Eq. (18) shows clearly that the dependence of χ on $\cos^2(\phi)$ of the superparamagnetic state (first term) is orthogonal to the $\sin^2(\phi)$ dependence of χ in the stable single-domain state (second term). In an anisotropic assemblages the prevalence of either χ_{SP} or χ_F will result in a different direction of the AMS maximum axis and of the AMS ellipsoid shape, going from the inverse pattern of a stable single-domain to normal pattern predicted for superparamagnetic grains. This is shown in Fig. 3 by plotting $\chi(\phi)$ for different grains with increasing $K_u v/k_b T$ ratios. In stable single-domain grains ($K_u v/k_b T > 18$ at the 100 Hz frequency) $\chi(\phi)$ is largest at $\phi = \pi/2$. On the other hand, $\phi = 0$ increases and soon became dominant upon rising $K_u v/k_b T$. The transition from inverse to normal AMS occurs over a narrow range of $K_u v/k_b T$ values corresponding to the onset of superparamagnetic effect. Due to their much higher susceptibility, even small amounts of superparamagnetic grains are likely to dominate the total susceptibility signal, becoming the main AMS carriers in samples where grain sizes are not strictly confined to the stable single-domain range.

3. Comparison with Experimental Data

Natural obsidian samples taken from different localities (Lipari Is., Palmarola Is. and Sardinia) and flows, have been used to test the normal AMS pattern of superparamagnetic magnetite particles predicted by the theory. Volcanic glasses are a well-suited testing material, since they contain very fine-grained iron oxides. Furthermore, it is possible to select samples with negligible contributions from non-SD particles. Obsidian samples are often very anisotropic, due to the alignment of ferrimagnetic inclusions along the flow direction

[*Canõń-Tapia and Castro*, 2004]. Because of the dominant magnetite mineralogy, and the abovementioned properties, obsidians can be used to test if the inverse AMS pattern of the stable single-domain is dominated by the normal AMS pattern of superparamagnetic particles.

Obsidian samples have been selected on the basis of mineralogy and grain size considerations derived from standard rock-magnetic measurements. The acquisition of isothermal remanent magnetization (IRM) at room (∼300K) and liquid nitrogen (77K) temperature was used to retrieve the contribution of superparamagnetic particles and investigate the magnetic mineralogy. The IRM was acquired with a pulse magnetizer and measured measured with a 2G DC-SQUID cryogenic magnetometer. Comparison of measurements at 77K and 300K (Fig. 4) shows that all selected obsidian samples have a large superparamagnetic contribution with a ratio IRM_{77K} to IRM_{300K} of ~ 2. The IRM acquisition for both low- and room-temperature curves is compatible with a predominant magnetite mineralogy, while the fraction of remanent magnetization acquired at field higher than 300 mT could be tentatively explained with strong magnetostriction or by partially oxidized magnetite grains. Samples SB2 and Palmarola shows higher saturation field at 77K that could count for the larger magnetocrystalline anisotropy of the monoclinic phase below the Verwey transition temperature [*Abe et al.*, 1976] or strong magnetostriction in the smaller grains.

IRM results are supported by hysteresis loops (Fig. 5), which were measured with Princeton Instrument vibrating sample magnetometer equipped with a cryostat for low temperature measurements at 80K. Low-temperature loops have thicker hysteresis loops and higher remanences compared to room temperature, as expected from theoretical models [*Lanci and Kent*, 2003], confirming presence of a large superparamagnetic fraction. The increased coercivity of samples SB2 and Palmarola, seen with IRM_{77K} acquisition curves, is also visible in the hysteresis loop measured at 80K, which is not saturated in the 0.7 T maximum measurement field. However, the hysteresis loops do not shows the constricted shape characteristic of a mixture of minerals with distinct (bi-modal) coercivity spectra, such as magnetite and hematite, suggesting a monodispersed coercivity spectrum end corroborating the hypothesis of monoclinic phase or strong magnetostriction of the SP grains.

The absence of a significant fraction of magnetization carried by multi-domain grains was verified by letting the samples cross the Verwey transition [*Verwey*, 1939]. The switch between cubic and monocline lattice remove the remanence carried by magneto-crystalline anisotropy, hence carried by multi-domain grains as well as equidimentional single domain particles [e.g., *Muxworthy and McClelland*, 1999]. This was performed by cooling the specimens at 77K applying a saturating field of 2 T and let them warm up to 300K and, the opposite, saturating the samples at 300K and measuring them after cooling at 77K. The presence of the Verwey transition was observed in other obsidians samples from the same flows that had a significant contribution of multi-domain grains and were, therefore, rejected for the purpose of this study. In the selected samples instead, both up-temperature and down-temperature measurements gave very similar magnetization slightly lower than the room temperature measurements. Results are shown in Fig. 6 and compared with the remanences at 300K and 77K, summarizing the negligible contribution of multi domain and large contribution of superparamagnetic grains that characterize these samples.

AMS measurements were performed using a KLY-3 Kappa Bridge and the 15 positions protocol, while the anisotropy of isothermal remanent magnetization (AIRM) was measured, on the same specimens, with a JR6 spinner magnetometer using a 12 positions protocol. The AIRM remanence was acquired applying a magnetic field of 20 mT to the samples, which were AF demagnetized before the next IRM along a different direction. The relatively low field was used because experimental studies have demonstrated the equivalence of anisotropy of thermal remanence with the low-field AIRM [*Stephenson et al.*, 1986], which became a standard procedure in rock magnetism. However, limited to the Lipari obsidians, we have tested the correspondence of AIRM acquired at 20 mT and 100 mT fields, which have virtually identical directions.

The directions of AMS and AIRM eigenvectors and the *Flinn* [2001] anisotropy parameters are plotted in Fig. 7. There are no practical differences between the direction of the principal axes of AMS and AIRM directions, indicating that all samples have a normal AMS pattern with the maximum susceptibility aligned with the preferential direction of the particle's easy axis indicated by the AIRM. The larger differences in the direction of the maximum anisotropy axes (about 20°) are observed in the SB2 and Palmarola specimens. The Flinn diagram shows similar degrees on anisotropy and similar shapes for AIRM and AMS. The AMS is better clustered and slightly less anisotropic than AIRM. This is a common experimental result [e.g. *Stephenson et al.*, 1986] that can be explained by the fact that AMS combines the inverse contribution of the stable single-domain grains with the predominant normal AMS of superparamagnetic grains.

4. Conclusions

We have described a simple model of magnetic susceptibility for uniaxial superparamagnetic and stable single-domain particles based on the theory of stochastic resonance. This model emphasizes the dependence of the susceptibility on the particle's orientation and in particular it shows that stable single-domain and superparamagnetic particles possess orthogonal maximum susceptibility axes. This means that in an ensemble of mixed stable single-domain and superparamagnetic particles with a preferential orientation, the AMS pattern can drastically change as function of grain size distribution, anisotropy constant or even measurement frequency and temperature, ranging from an oblate inverse pattern with the minimum eigenvalue along the field direction, which is characteristic of the stable single-domain state [e.g., *Rochette et al.*, 1992], to a prolate pattern with maximum eigenvalue along the field direction predicted for superparamagnetic.

Because of this complex behavior a quantitative interpretation of the AMS pattern in uniaxial magnetite/maghemite bearing rock seems rather complicated. In ensembles of identical particles, there is sharp temperature dependence of the AMS pattern that is related to the switch from stable single-domain to superparamagnetic, however in natural samples with a wider distribution of $K_u v/k_b T$ ratios the transition can be more gradual. In principle, this could be computed from (18) if the grain-size and coercivity distributions were accurately known, but this is unlikely in natural samples. Even if a complete inversion of the AMS pattern does not occur because, for instance, the contribution of superparamagnetic grains is not large enough, the strong dependence of AMS from the $K_u v/k_b T$ ratio will introduce a bias in the AMS eigenvalues complicating their interpretation. It is suggested that AMS measurements at different frequencies could help recognizing the effect of superparamagnetic grains on AMS pattern.

Theoretical predictions are confirmed by results from obsidians samples, which have a large superparamagnetic and negligible multi-domain grains population, and shows that AMS axes are consistent with the AIRM axes, hence maximum anisotropy axes are align to the easy taxes. Other similar examples can be found in the literature *Canõń-Tapia and Castro* [2004]; *Canõń-Tapia and Caŕdenas* [2012] for instance, have reported cases of obsidians where the magnetic mineralogy was identified as a mixture of single-domain magnetite with a substantial contribution of the superparamagnetic fraction and none of them shows a inverse AMS pattern.

Our theory give an alternative explanation to the common case of coinciding AMS and AIRM axes, which are usually interpreted as due to the presence of multi-domain grains dominating the AMS [e.g., *Tarling and Hrouda*, 1993] and justify why the inverse AMS is very rarely, if ever, observed in natural samples. In fact, inverse AMS is actually restricted to the true stable single-domain state having a narrow range of grain sizes in magnetite and maghemite. In natural samples stable single-domain particles are most often combined with superparamagnetic and/or multi-domain particles, which are likely to dominate the inverse AMS pattern either because of the much higher susceptibility of the former or because larger volumes of the latter.

Acknowledgments. E. Ferrara (INRIM) is acknowledged for the hysteresis measurements. We thank V. Shcherbakov, R. Egli, A. Newell and B. Moskowitz for their comments and suggestions. Supporting data are available from the corresponding author (luca.lanci@uniurb.it). This work was supported by University of Urbino and DiSBeF research project 2014.

References

Abe, K., Y. Miyamoto, and S. Chikazumi (1976). Magnetocrystalline anisotropy of low temperature phase of magnetite, Journal of the *Physical Society of Japan*, *41*, 1894–1902.

Bertotti, G., (1998), *Hysteresis in Magnetism. For Physicist, Material Scientists and Engineers*, Academic Press series in Electromagnetism. Academic Press, San Diego.

Brown, W. F. Jr., (1963), Thermal Fluctuations of a Single-Domain Particle, *Phys. Rev.*, *130*, 1677.

Canõń-Tapia, E. and Caŕdenas, K., (2012), Anisotropy of magnetic susceptibility and magnetic properties of obsidians: volcanic implications, *International Journal Earth Science (Geol. Rundsch)*, *101*, 649–670

Canõń-Tapia E., and Castro J., (2004), AMS measurements on obsidian from the Inyo Domes, CA: a comparison of magnetic and mineral preferred orientation fabrics. *J. Volcanol. Geotherm Res.*, *134*, 169–182.

Coffey W. T., Crothers D. S. F., Dejardin J. L., Kalmykov Yu. P., Raikher Yu. L., Stepanov V. I. and Titov S. V., (2001), Noise-induced resonances in superparamagnetic particles. *Material Science Forum*, *373–376*, 125–128.

Egli R., (2009), Magnetic susceptibility measurements as a function of temperature and frequency. I: Inversion theory. *Geophys. J. Int.*, *177*, 395420, doi:10.1111/j.1365-246X.2009.04081.x.

Flinn D., (1962), On folding during three dimensional progressive deformation. *Geological Society London. Quart.*, *118*, 385–433.

Gammaitoni, L., Hänggi, P., Jung, P. and Marchesoni F., (1998), Stochastic resonance. *Reviews of Modern Physics*, *70*(1), 223–287.

García-Palacios, J.L., (2000), On the statics and dynamics of magneto-anisotropic nanoparticles. *Adv. Chem. Phys.*, *112*, 1–210.

Jones, D. H. and Srivastava, K. K. P., (1989), A re-examination of models of superparamagnetic relaxation. *J. Magn. Magn. Mater.*, *78*, 320–328.

Kalmykov Yu. P., Raikher Yu. L., Coffey W. T. and Titov S. V., (2005), Stochastic resonance in single-domain nanoparticles with cubic anisotropy. *Phys. Solid State*, *47*(12), 2325–2232.

Lanci, L., and Kent D. V., (2003), Introduction of thermal activation in forward modeling of SD hysteresis loops and implications for the interpretation of the Day diagrams, *J. Geophys. Res.*, *108*(B3)(2142).

Lanci, L., (2010), Detection of multi-axial magnetite by remanence effect on anisotropy of magnetic susceptibility, *Geophys. J. Int.*, *181*, 1362–1366.

McNamara, B. and Wiesenfeld, K., (1989), Theory of stochastic resonance. *Phys. Rev. A*, *39*, 4854–4869.

Moskowitz, B.M., Frankel, R.B., Walton, S.A., Dickson, D.P.E., Wong, K.K.W., Douglas, T. and Mann, S., (1997). Determination of the preexponential frequency factor for superparamagnetic maghemite particles in magnetoferritin, *J. Geophys. Res.*, *102*(22) 671–680.

Mullins, C. E. and Tile, M. S., (1973), Magnetic viscosity, quadrature susceptibility, and frequency dependence of susceptibility in single-domain assembly of Magnetite and Maghemite. *J. Geophys. Res.*, *78*(5), 804–809.

Muxworthy A. and McClelland E., (1999), Review of the low-temperature magnetic properties of magnetite from a rock magnetic perspective. *Geophys. J. Inter.*, *140*, 101–120.

Néel, L., (1949), Théorie du trainage magnétique des ferromagnétiques en grains fins lavec applications aux teries cuites, *Annals of Geophysics*, *5*, 99–136.

O'Reilly, W., (1984), *Rock and mineral magnetism*, Chapman and Hall, New York.

Raikher Yu. L., Stepanov V. I. and Fannin P. C., (2003), Stochastic resonance in a superparamagnetic particle. *J. Magn. Magn. Mater.*, *258*, 369–371.

Rochette P., Jackson M. and Aubourg C., (1992), Rock magnetism and the interpretation of anisotropy of magnetic susceptibility, *Reviews of Geophysics*, *30*, 209–226.

Shcherbakov, V. P. and Fabian K., (2005), On the determination of magnetic grain-size distribution of superparamagnetic particle ensembles using the frequency dependence of susceptibility at different temperatures, *Geophys. J. Int.*, *162*, 736–746.

Stephenson, A., Sadikun, S. and Potter, D. K. (1986), A theoretical and experimental comparison of the anisotropies of magnetic susceptibility and remanence in rocks and minerals, *Geophys. J. Int.*, *84*(1), 185–200, doi:10.1111/j.1365-246X.1986.tb04351.x .

Stoner, E. C., and Wohlfarth E. P., (1948), A mechanism of magnetic hysteresis in heterogeneous alloys, *Philosophical Transactions of the Royal Society London*, *240*(826), 599–642.

Svedlindh, P., Jonsson, T. and Garca-Palacios, J.L., (1997), Intra-potential-well contribution to the AC susceptibility of a noninteracting nano-sized magnetic particle system.

J. Magn. Magn. Mater., *169*(3), 323–334

Tarling D.H., Hrouda F. (1993), *The Magnetic Anisotropy of Rocks*. Chapman & Hall, London, UK.

Vernay, F., Sabsabi, Z. and Kachkachi, H. (2014), AC susceptibility of an assembly of nanomagnets: combined effects of surface anisotropy and dipolar interactions. *Phys. Rev. B*, *90*, 094416.

Verwey E., (1939), Electronic conduction of magnetite (Fe_3O_4) and its transition point at low temperature. *Nature 44*, 327–328.

Worm, H.-U., (1998), On the superparamagnetic–stable single domain transition for magnetite, and frequency dependence of susceptibility, *Geophys. J. Int.*, *133*, 201–206.

Figure 1. (a) Geometrical description of the elements for uniaxial particles. (b) Sketch of the double-well potential $E = K_u\, v \sin^2 \phi$. In absence of periodic field H, the minima are located at a distance of π radiant and separated by a potential barrier with height $E_b = K_u\, v$. In the presence of periodic field H, the double-well potential is tilted back and forth raising and lowering the potential barriers of the right and the left well, respectively. In the figure the effect of the magnetic field on the potential E is exaggerated for clarity.

Figure 2. Amplitude of $\langle n_+(t) \rangle$ as function of the temperature for different orientation orientations ϕ (in radiants) of the easy-axis. Peak-shaped function results from the effect of stochastic resonance. The stochastic resonance effect is maximum for grain with easy-axis along the field direction and null for grain with easy-axis orthogonal to the field direction, hence no superparamagnetic susceptibility is expected for the latter.

Figure 3. (a) Susceptibility $\chi(\phi)$ (in logarithmic scale) as function of the easy axis orientation ϕ. Lines of different colors represent grains with increasing $K_u v/k_b T$ ratios ranging approximately from 15 to 25, from superparamagnetic to stable single-domain. Stable single-domain grains dominated grains are characterized by maximum $\chi(\phi)$ at $\phi = \pi/2$, hence showing the characteristic inverse AMS patten. On the contrary, at smaller $K_u v/k_b T$ ratio, the the susceptibility became much larger at $\phi = 0$ and exhibit the normal AMS pattern expected when superparamagnetism is dominant. (b) Susceptibility χ averaged over uniformly distributed ϕ as a function of the $K_u v/k_b T$ ratio. Black circles correspond to the same set of instances shown in panel (a). Other parameters used in the plot are $M_s = 480000$ A/m, and frequency $2\pi\,\omega = 100$ Hz.

Figure 4. IRM acquisition of obsidian samples at 300K (closed symbols) and 77K (open symbols). Palmarola and SB2 specimens show an increased coercivity at low temperature suggesting a higher degree of oxidation in superparamagnetic grains.

Figure 5. Hysteresis loops of obsidian samples. Thin blue line represent measurements at 80K and red thicker line represent room temperature measurements.

Figure 6. Low temperature (77K), room temperature (300K), up-temperature and down-temperature Verwey transition of obsidian samples. Differences between different measurements estimates the superparamagnetic, stable single-domain and multi domain contribution as described in the text.

Figure 7. Pattern of principal axes of AMS and AIRM in the obsidian samples (a) Flinn diagram [*Flinn*, 2001] indicating a generally try-axial shape of the anisotropy ellipsoids with similar values for AMS and AIRM. (b) Equal-area plot (lower hemisphere) of the directions of the principal anisotropy axes.