

Low-temperature magnetic anomaly in magnetite

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We have studied experimentally the responses of high-quality single crystals of stoichiometric synthetic magnetite to applied weak dc and ac magnetic fields in the range of 6–60 K, far below the Verwey transition. The results can be compared to so-called magnetic after effects (MAE) measurements, which are the most extensive magnetic measurements of magnetite at these temperatures. We present a novel point of view on the relaxation phenomena encountered at these temperatures—the low-temperature anomaly, addressing the striking difference between the results of conventional ac susceptibility measurements and those accompanying MAE measurements, i.e., periodic excitations with strong magnetic pulses. We also draw a connection between this anomaly and the so-called glasslike transition, and discuss possible mechanisms responsible for these effects.

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I. INTRODUCTION

Unusual physical properties of magnetite (Fe_3O_4), the oldest known magnetic material, gave birth, among others, to Mott's model of metal-insulator transition (MIT) and to the variable-range hopping mechanism of electrical conductivity.^{1,2} Many physical properties of the material were apparently explained by a relatively simple model of charge ordering of Fe^{2+} and Fe^{3+} cations below the so-called Verwey temperature $T_V \approx 123$ K at which the MIT together with a structural transition occur (the Verwey model of charge ordering^{3–5}). And although in recent studies^{6–9} the question of the strict meaning of Verwey-like charge ordering and the low- T atomic structure is solved, the exact mechanism of the Verwey transition is still in dispute, and the phenomena below $T = 50$ K are far from being well understood. These phenomena are treated in our paper.

Magnetite is ferrimagnetic with a Néel temperature $T_N \approx 860$ K; it forms a spinel-like cubic lattice at high temperatures (≈ 1400 K), which gradually transforms from random spinel to inverse-spinel cubic at room temperature,¹⁰ and discontinuously transforms to monoclinic Cc at T_V , as was determined by x-ray diffraction^{8,11} and NMR.¹² Other measurements, however, suggest even lower crystal symmetry (magnetoelectric measurements,¹³ appearance of ferroelectricity,¹⁴ and x-ray topography measurements).¹⁵

In this paper we focus on the behavior of magnetite well below T_V , especially its magnetic properties in weak ac and dc fields. We have noticed a striking difference between the ac susceptibilities accompanying magnetic after-effect studies (MAE, disaccommodation effect) of stoichiometric magnetite¹⁶ and the susceptibilities measured by other techniques (e.g., an inductive bridge method¹⁷) below 35 K. More specifically, the notion of the anomaly stems from the bifurcation of the $\chi'(T)$ dependence at low temperatures (see inset of Fig. 1), where the upper curve represents

an MAE measurement and the lower represents a classical result [e.g., a superconducting quantum interference device (SQUID) measurement; a notable exception is the result¹⁸ of ac susceptibility studies]. Bearing in mind the specifics of MAE measurements, we devised a series of experiments with the aim of explaining these discrepancies.

II. SAMPLES

The samples used in our experiments were high-quality single crystals of synthetic magnetite grown in the laboratory of J.M. Honig of Purdue University (samples denoted H) and by V.A.M. Brabers of Eindhoven University of Technology (samples denoted B). The samples B were grown by a floating zone technique.¹⁹ The samples H were prepared by a skull melter technique.²⁰

Namely, the sample B1 was annealed to a stoichiometric composition and cut to the shape of a cylinder 5 mm in diameter and 4 mm high. The cylinder axis is parallel to the crystallographic c axis, direction (001). This sample was also used for NMR measurements.²¹

The sample H1 was a prism with dimensions $2.1 \times 2.3 \times 3.1$ mm³ (the longest edge along (001)) annealed for stoichiometry.²² Since the annealing procedure was different from that for B1, it resulted in a different defect pattern, as measured by the MAE technique.²³ This sample was also used for ac susceptibility measurements.¹⁸ The sample H2—a platelet of irregular shape roughly 8×13 mm² and thickness of 1.8 mm—although not annealed, was apparently close to stoichiometry due to preparation conditions.²⁰ Thus, three samples, very close to stoichiometry, but with possibly a different defect pattern, were measured. For comparison, the measurements were also performed on the deliberately non-stoichiometric sample, H3, a roughly pyramidal single crystal of $\text{Fe}_{3(1-\delta)}\text{O}_4$ with $\delta = 0.002$ and dimensions approximately $1.5 \times 1.5 \times 2.0$ mm³.

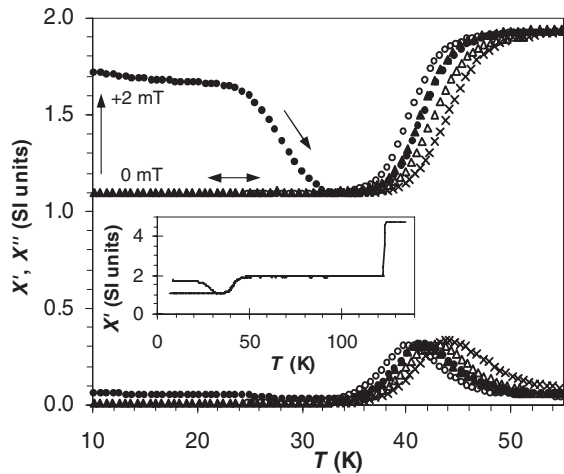


FIG. 1. Real part (top symbols) and imaginary part (bottom symbols) of complex ac susceptibility, H1 sample, as a function of temperature, ac field amplitude $5 \mu\text{T}$, ac field frequency 1.6 Hz (\circ), 3.1 Hz (\bullet, \blacktriangle), 6.3 Hz (\triangle), and 12.5 Hz (\times). The anomaly (\bullet) was excited by increasing the dc field by 2 mT at 10 K . The inset: overall temperature dependence of real susceptibility in weak magnetic field, $\mu_0 H_{ac} = 10 \mu\text{T}$ at 6.3 Hz .

III. TECHNIQUE

The magnetic properties were measured using a noncommercial, continuously operating SQUID magnetometer with an immobile sample, where the magnetic field is generated by a superconducting solenoid operating in nonpersistent mode, and the variations of the magnetic moment of the sample are read continuously using a SQUID.²⁴ The workspace, including the superconducting solenoid, superconducting gradiometer, SQUID, thermometers, heater, and the sample, was magnetically shielded, using both a superconducting (lead) can and soft magnetic material surrounding the cryostat. The achieved spectral density of magnetic moment was $\approx 17 \text{ pA m}^2 \text{ Hz}^{-1/2}$, and the residual field was less than $2 \mu\text{T}$ inside the sample chamber. The sample, mounted on a sapphire holder, was in a ^4He gas environment at atmospheric pressure and was subjected to a time-varying magnetic field of maximum intensity of about 20 mT . The spectral response of the magnetometer was flat from dc up to about 150 Hz .

Both the applied field generation and the sample response acquisition were carried out by a dedicated computer equipped with appropriate analog converters. In typical susceptibility measurements reported here, the applied field was varied sinusoidally, the SQUID signal (sampled at 6.4 kHz) was processed by fast Fourier transform, and the results were expressed as a set of complex harmonic susceptibilities. With weak driving ac fields the sample response was linear and only the fundamental susceptibility was considered, the higher harmonics being negligible.

IV. RESULTS

When a single crystal of stoichiometric magnetite is cooled from room temperature down to a few kelvin in the absence of a dc magnetic field and in a weak ac field, the thermal

dependence of its complex ac susceptibility $\chi_{ac} = \chi' - i\chi''$ is remarkably simple (see inset of Fig. 1). Above the Verwey transition the value of χ' may reach as high¹⁷ as 10^3 (SI units), especially near the easy axis reorientation temperature,²⁵ but due to finite sample size the measured value is limited to $1/N$, N being the demagnetizing factor. Below T_V the crystal symmetry changes and new (and large) components of magnetocrystalline anisotropy energy appear,²⁶ $|\chi_{ac}|$ reduces to the order of unity,¹⁷ and demagnetizing effects can be neglected in a qualitative approach. Further below T_V , in the range $60\text{--}35 \text{ K}$, a frequency-dependent thermally activated process, denoted here as a “glasslike transition,”²⁷ occurs after. Both the strong frequency dependence of this transition and the accompanying peak in absorption (the imaginary part, χ'') agree well with Debye’s relaxation model of thermally activated magnetic moments. Below about 30 K , when these moments are frozen in for all practical frequencies, we measured and described a manifestation of relaxation processes in magnetite, which we call the *low-temperature anomaly* (Fig. 1).

The anomaly is described as follows: During cooling of a stoichiometric magnetite in a “normal” way (i.e., in a relatively weak magnetic field without abrupt changes—ac field up to $100 \mu\text{T}$ and dc field up to several mT), χ' reaches its lowest value below the glasslike transition (further denoted as the “frozen” state) and retains this value down to the lowest temperatures. Also, χ'' is nearly zero in this region. Upon subsequent warming at the same conditions, the same $\chi(T)$ is observed (symbols “ \blacktriangle ” in Fig. 1). However, when an abrupt disturbance is applied at low temperature (e.g., step change of dc field by several millitesla), χ' jumps to a new higher steady value—the anomaly is “excited.” Upon subsequent warming of such an excited sample, $\chi(T)$ relaxes back to the “frozen” state value before the glasslike transition takes place (symbols “ \bullet ” in Fig. 1). This universal behavior of stoichiometric magnetite was found to be insensitive to the ac field frequency and amplitude (provided it is relatively weak, up to about $100 \mu\text{T}$) and the absolute intensity of dc magnetic field (within our accessible range of $+/- 20 \text{ mT}$). Only the magnitude and character of the excitation event (even a short pulse of several millitesla amplitude may excite the anomaly) determine the extent to which the anomaly is excited.

To further explore this behavior, we have performed an experiment in which the dc field was swept in a triangular fashion ($0 \rightarrow +1 \text{ mT} \rightarrow 0 \rightarrow -1 \text{ mT} \rightarrow 0$ with a period of 120 s) with a superimposed weak ac field at several fixed temperatures (Fig. 2). Apparently, at 35 K the sample maintained the “frozen” state, regardless of the changing dc field [curve (c)]. At lower temperatures the change of dc field causes χ' to increase, but in this case the process is largely reversible, and the sample returns close to the “frozen” state after removal of the dc field [curves (a), (b)]. With other samples (H2, B1) or with bigger changes of the dc field the process is irreversible.

Changes of spontaneous magnetization of the magnetite sample during the transition are depicted in Fig. 3. Although more dependent on the thermal and magnetic history of the sample, the magnetization shows several general features: (i) no dramatic changes of magnetization occur in the region of glasslike transition, neither on cooling nor on warming the sample; (ii) if the anomaly was excited at low temperature

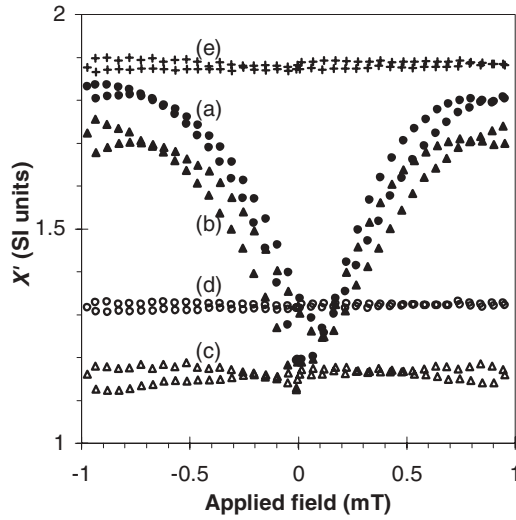


FIG. 2. The dc field dependence of ac susceptibility at various temperatures: (a) 10 K, (b) 28 K, (c) 35 K—the “frozen” state, (d) 43 K, and (e) 50 K—above the glasslike transition. The field was swept continuously in the range of ± 1 mT in a triangular fashion, the whole cycle taking 120 s. The susceptibility was measured simultaneously with an ac field of $20 \mu\text{T}$ at 6 Hz, H1 sample.

the sample fully accommodates to the new conditions by a change of spontaneous magnetization that takes place at higher temperature than the relaxation of ac susceptibility (to the “frozen” state); and (iii) the magnitude of the change of spontaneous magnetization is rather low, in this case only about 10% of the total response of the sample to the step change of the applied dc field.

The relaxation of the anomaly was also found to depend on the rate of sample warming: the lower the rate, the lower the

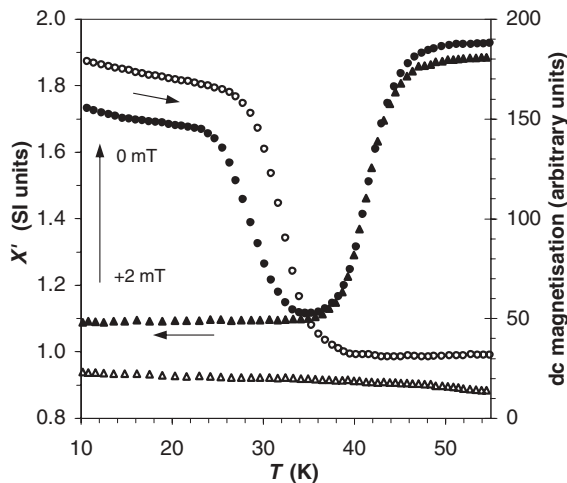


FIG. 3. Real part of ac susceptibility (full symbols) and accompanying changes of spontaneous dc magnetization (open symbols), H1 sample, as a function of temperature, ac field amplitude $5 \mu\text{T}$ at 6.3 Hz. The anomaly was excited by decreasing the dc field by 2 mT at 10 K. [The units of magnetization are essentially A/m, except for an additive constant—an offset—which is unknown due to the working principle of a SQUID. This offset is also different for cooling (Δ) and warming (\circ).]

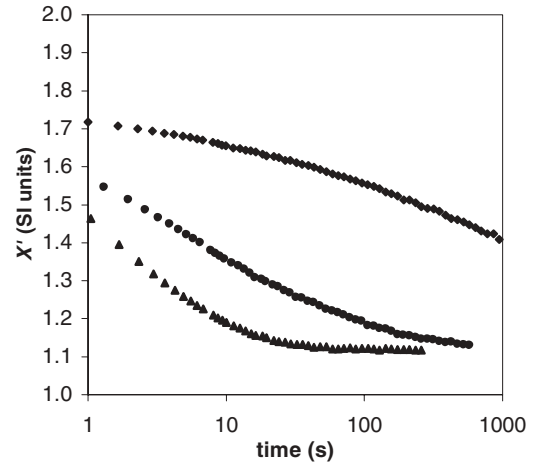


FIG. 4. Relaxation of the real part of ac susceptibility after a 2-mT step of applied magnetic field at 25 K (top symbols), 30 K, and 33 K (bottom symbols). H1 sample, ac field amplitude $5 \mu\text{T}$ at 6.3 Hz.

temperature at which the “frozen” state is reached. This feature is further explored in relaxation measurements where a step change of magnetic field is applied at a defined temperature in the range of 10–35 K and the time dependence of the ac susceptibility is recorded (Fig. 4).

The properties of several samples (including a nonstoichiometric single crystal) were measured and the results summarized in Table I. Note that in the samples departing from perfect stoichiometry, the glasslike transition shifts quickly to lower temperatures and the anomaly cannot be observed, even at lowest attainable temperature (about 6 K in the current setup).

V. DISCUSSION

The microscopic origin of the observed phenomena cannot be determined unambiguously from the experimental findings. However, we present several arguments suggesting that the measured changes of susceptibility of magnetite below T_V arise solely from the changes of the mobility of *domain walls*: (i) both the saturation magnetization ($4 \mu_B$ per Fe_3O_4 formula agrees well with the experimental value of 0.5 MA/m)²⁸ and

TABLE I. A summary of transition temperatures (the Verwey transition, the glasslike transition T_g at 6 Hz, and the temperature of relaxation of the anomaly T_a , warming rate 1 K/m) of measured samples. The ac amplitude was $10 \mu\text{T}$, and the anomaly was excited by a dc field step of 2 mT at 10 K. T_g and T_a are defined as inflection points of the $\chi'(T)$ curve. The differences in the magnitude of the anomaly (in percent of the magnitude of the glasslike transition) are mainly caused by different demagnetizing factors of the samples. H3 is nonstoichiometric with $\delta = 0.002$.

Sample	T_V (K)	T_g at 6 Hz (K)	T_a (K)	Anomaly magnitude
H1	122.2	41.7	27.2	20%
H2	122.0	40.3	23.0	80%
B1	121.5	36.4	18.0	50%
H3	117.5	21.0	—	—

the magnetocrystalline anisotropy (the largest component²⁶ is about 0.25 MJ/m³) are approximately constant below T_V . Thus the susceptibility arising from the rotation of domain magnetization should not depend on temperature. Moreover (ii) this susceptibility is about an order of magnitude lower²⁹ than the measured susceptibility. (iii) A notably similar effect was observed seven decades ago in iron with carbon or nitrogen impurities at 250 K,³⁰ attributed to diffusion of the impurities to the domain walls in order to accommodate magnetostrictive strain. These impurities then act as potential minima that hinder the domain wall motion in a certain temperature range.

Similar measurements of high-purity single-crystal magnetite¹⁸ at low temperatures also suggest that magnetic domain walls are responsible for the observed effects. The authors also eliminated the effect of structural domain walls by detwinning the sample in strong magnetic fields. However, in those measurements the anomaly always appears in the “excited” state, probably due to the high amplitude of ac magnetic field used in their experiments (≥ 100 μ T).

To explain the low-temperature anomaly, we hypothesize the existence of pinning centers that create a net of potential minima for the domain walls. Starting from the “frozen” state at 35 K (see Fig. 1), all domain walls lie in these minima, and a weak applied ac field induces only a small response of the sample magnetization χ' . According to the assumptions³¹ about domain wall parameters, we may assume that an ac field with amplitude $\mu_0 H_{ac} \leq 100$ μ T is weak enough to cause domain wall displacement that is much less than the wall thickness. This process is reversible and, if the pinning centers are stationary, no energy is dissipated (χ'' is also small). But as the temperature is elevated the pinning centers are no longer fixed, thermal activation allows them to follow the displacing walls, and energy is dissipated. This process gives rise to the frequency-dependent Debye-like relaxation at 40–50 K as described previously.²⁷ Above 60 K the pinning centers move freely with the domain walls, the potential minima are not effective, and χ' is large.

To complete the explanation of the anomaly, let us again start from the “frozen” state at 35 K, where the domain walls reside in their potential minima. This state is preserved when the sample is further cooled to the lowest temperature (6 K in this experiment). Now the anomaly can be “excited,” e.g., by changing the dc component of the applied magnetic field by a sizable amount (several millitesla). The domain walls are pulled from their potential minima and χ' rises [see curve (a) in Fig. 2]. When this “excited” sample is warmed gradually, the hypothetical pinning centers start to move to their new equilibrium positions, i.e., into the domain walls, new potential minima appear, and the susceptibility approaches the “frozen” state. This gives rise to a strongly temperature-dependent relaxation of the ac susceptibility (see Fig. 4), and the very same relaxation is responsible for the large peak in MAE spectra at about 30 K.¹⁶

The connection between our results and the MAE spectra is very intimate for two reasons: (i) both methods are based on ac magnetic susceptibility measurements after some excitation with a strong magnetic field (we excite the sample only once at the lowest temperature, whereas during a MAE measurement the magnetic pulse is applied periodically), and (ii) the characteristic times of both methods are similar. It is important to

note that there are in fact two characteristic times incorporated in these techniques. One is determined by the frequency of probing magnetic field (1 kHz in MAE measurements and 1–100 Hz in our measurements, corresponding to 1 and 10 ms to 1 s, respectively). The other characteristic time is the isochronal time of the MAE experiment (1–180 s); in our experiments it is determined by the rate of sample warming, and although it is not strictly defined, it is of the order of seconds to hundreds of seconds. The above-mentioned peak in MAE spectra around 30 K is attributed by the authors¹⁶ to “*intraionic* thermal interlevel excitations,” i.e., an excitation of the “free” electron of an individual Fe²⁺ ion from the ground state across a gap that appears due to the energy-level splitting in a trigonal crystal field. Our explanation, on the other hand, takes into account diffusion phenomena.

The microscopic nature of the hypothesized pinning centers remains unclear. However, some arguments can be summarized to elucidate the underlying mechanism: (i) a similar effect in iron³⁰ is ascribed to the diffusion of impurities (at concentration of 0.01%). This most definitely will *not* be the case of magnetite, as even minute concentration of impurities or structural defects shifts the glasslike transition to lower temperatures (in accordance with MAE results³²) and destroys the low-temperature anomaly (see Table I). Also, relaxation effects of vacancies and impurities in magnetite are expected well above T_V . (ii) The crystallographic domains that appear when cooling magnetite single crystal through T_V have a substantial impact on the magnetic susceptibility,¹⁸ but their structure is fixed at low temperature (easy axis switching can be induced by much larger fields close below T_V , Ref. 33) and the structural domains themselves cannot account for the observed phenomena. (iii) One plausible explanation is the interplay between the structural, magnetic, and ferroelectric domain structure, as spontaneous polarization was identified in magnetite thin films below 40 K,³⁴ and the coupling between magnetic and dielectric properties of magnetite was identified long ago.¹³ However, a comparison of relative sizes of structural, magnetic and ferroelectric domains that might support this explanation cannot be easily done, as the properties of ferroelectric domains in bulk magnetite are currently unknown and the size of magnetic domains was reported in the range 30–100 μ m.^{15,35} In thin samples³⁶ the size of both structural and magnetic domains is in the range 1–10 μ m, with possibly even smaller twin domains.

Other experimental findings that may be important with respect to the low-temperature anomaly are the anomalous behavior of dielectric susceptibility³⁷ and significantly shortened NMR spin-spin relaxation times,²¹ both observed in magnetite at similar temperatures.

VI. CONCLUSION

We have measured and described a novel manifestation of relaxation phenomena in high-quality single crystals of stoichiometric synthetic magnetite in weak low-frequency magnetic fields. The largely unnoticed discrepancy between ac susceptibilities accompanying magnetic after-effect measurements and the results of conventional experiments (performed on top-quality synthetic samples) was consistently explained

as resulting from the interaction between magnetic domain walls and pinning centers that can diffuse toward the domain walls at elevated temperatures (above about 25 K). A single diffusion process thus manifests itself both as a frequency-dependent glasslike transition above 35 K and time-dependent susceptibility relaxation below 35 K, the characteristic experiment time scales being the frequency of the ac magnetic field and the rate of sample warming, respectively.

However, the microscopic origin of the pinning centers remains unclear. Impurities and structural defects that can give rise to similar effects in pure iron³⁰ are ruled out, as even minute amounts of defects shift the glasslike transition quickly to lower temperatures and the anomaly disappears completely. The rigidity of structural domain walls at these temperatures and the results in strong fields¹⁸ make it evident that the interaction between structural and magnetic domains cannot

account for the observed effects. A process encompassing ferroelectricity is proposed, whose elucidation will require more profound experiments to be carried out, such as combined magnetic and transport measurements in strong electric field, or nonlinear susceptibility measurements by means of higher-order harmonic susceptibilities.

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