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Magnetic relaxation in spinel Mo-ferrite and Ti substituted Mo-ferrite

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Abstract. A compensation temperature of 138 K was observed in the temperature-dependent magnetization curves of $MoFe_2O_4$. Relatively slow magnetization relaxation characterized the transitions between different spin states (compensated and uncompensated). Large magnetic after effect was found in time-dependent magnetization curves after heating or cooling from different characteristic temperatures for different spin states. The magnetic relaxation was nearly independent on magnetic field, supporting the presence of spin states and no involvement of domain structure. For the Ti substituted $Mo_{0.6}Ti_{0.4}Fe_2O_4$ sample, there were a compensation at ∼100 K and a maximum of magnetization at ∼175 K. Similar results of anomalous magnetic relaxation was observed in Ti substituted Mo-ferrite ($Mo_{0.6}Ti_{0.4}Fe_2O_4$). If the $Mo_{0.6}Ti_{0.4}Fe_2O_4$ sample was heated from 100 K to 235 K, the time-dependent magnetization curve could be considered as a combination of two magnetic relaxation processes. However, if the sample was heated from 100 K to 295 K, the time- dependent magnetization curve became complex.

PACS. 75.60.Lr Magnetic aftereffects – 75.60.Ej Magnetization curves, hysteresis, Barkhausen and related effects – 75.50.Gg Ferrimagnetics

1 Introduction

Mo-ferrite ($MoFe_2O_4$) has many unique magnetic properties [1–3]. Mo-ferrite and its related materials have been investigated by many research groups [1–8]. The compound is weak magnetic with a Néel temperature of ∼350 K and a compensation temperature of around 160 K [1]. The valency distribution may be represented by the balance between the following reactions in the octahedral (B) and tetrahedral (A) sites: $Fe^{2+}{}_B + Fe^{3+}{}_A + Mo^{3+} \lambda\, Fe^{3+}{}_B + Fe^{2+}{}_A + Mo^{3+} \lambda\, Fe^{2+}{}_B + Fe^{2+}{}_A + Mo^{4+}$. The compensation temperature at around 160 K was explained by a Néel type ferrimagnetism [2,3].

Magnetic relaxation is a useful tool for the study of magnetization and demagnetization mechanisms. Magnetic relaxation has been observed in different magnetic materials, such as thermal excitation in magnetic hysteresis, change of magnetization in spin glass system and tunneling effect at low temperatures [9–11]. In the most magnetic relaxation studies, magnetic viscosity is measured as the change of magnetization as a function of time at a constant temperature after a variation of magnetic field. In this work, we have studied the spin re-arrangement around the compensation temperature of $MoFe_2O_4$. Slow magnetic relaxation was observed. This slow magnetic relaxation was temperature-dependent but not strongly dependent on field. Similar results were found for Ti substituted $Mo_{0.6}Ti_{0.4}Fe_2O_4$.

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2 Experiment

Two samples of the nominal compositions of Fe_2MoO_4 and $Fe_2Mo_{0.6}Ti_{0.4}O_4$ respectively were prepared by solid solution during heat treatment. The X-ray diffraction study showed that the sample consisted of single-phase cubic spinel. The detail of the sample preparation and structural characterization was reported [7,8]. The magnetization measurements were carried out with a vibrating sample magnetometer (Oxford Instruments) with a maximum magnetic field of 90 kOe in the temperature range from 5 to 300 K.

It has been found, that the samples studied in this work need a long time to reach equilibrium after heating or cooling. In this work, hysteresis loops (saturation magnetization, remanence and coercivity) were taken under equilibrium condition, *i.e.* after waiting for 5000 s after reaching the desired temperature. Temperature-dependent magnetization curves (M-T curves) were taken under a constant magnetic field (usually 60 kOe) with a constant heating or cooling rate of 3, 6 or 10 K/min.

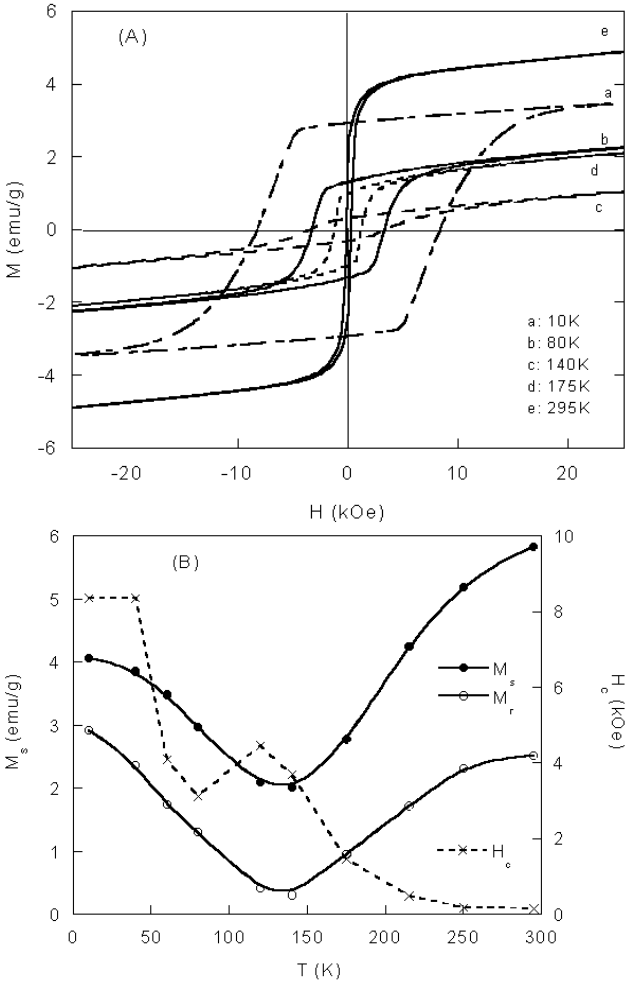

Fig. 1. Magnetic hysteresis loops taken at different temperatures (A). Saturation magnetization M_s, remanence M_r and coercivity H_c as a function of temperature for $MoFe_2O_4$(B).

Before the M-T curve was taken, the sample was under equilibrium condition at the initial temperature (waiting for 5000 s). For a time-dependent magnetization curve (M-t curve), the sample was firstly heated (or cooled) from a characteristic temperature (for a certain spin state) under a constant magnetic field (usually 60 kOe). The time-dependent magnetization curve (M-t curve) was then recorded under a constant temperature and constant magnetic field (usually 60 kOe) as a function of time.

3 Results and discussion

3.1 $MoFe_2O_4$

Figure 1 shows the hysteresis loops taken at different temperatures for $MoFe_2O_4$ (a), and their saturation magnetization M_s (measured at 60 kOe), remanence M_r and coercivity H_c (b). It is to note that the hysteresis loops were taken in equilibrium state, *i.e.* after waiting for 5000 s when reached the desired temperature. As reported previously [2,3], $MoFe_2O_4$ is weak-magnetic at room temperature. A clear hysteresis was observed at room temperature (Fig. 1A). Saturation magnetization M_s at room temperature was around 5 emu/g (Fig. 1B), corresponding to a magnetic moment of approximately 0.4 μ_B per formula. The magnetization was in a good agreement with the moment value reported [2,3]. The small magnetization is due to uncompensated iron moment because of hopping between Fe^{2+} and Fe^{3+} [1–3]. Magnetization decreased with decreasing temperature and reached a minimum at around 140 K. The remanence M_r had a similar trend to that of magnetization M_s with a minimum at around 140 K. A detailed study showed a minimum at 138 K with a remanence value approaching zero, indicating a compensation temperature. Similar results of the compensation temperature have been reported previously [1–3]. When temperature was below compensation temperature of 138 K, M_s increased with decreasing temperature (Fig. 1B).

Hysteresis loops taken at room temperature had a soft magnetic behavior, as shown by the low coercivity value. Coercivity H_c started to increase in the temperature range of 200–250 K, and reached the level of 3–5 kOe at temperatures around the compensation temperature. A further decrease in temperature till 60 K did not cause a significant change in coercivity (3–5 kOe). Coercivity jumped to 8.4 kOe when cooled to 40 K (Fig. 1). Coercivity remained constant when the sample was further cooled to 10 K. This result indicated hard magnetic properties when temperature was below the compensation temperature.

Figure 2 shows temperature-dependent magnetization (M-T curve) of $MoFe_2O_4$ measured under a magnetic field of 60 kOe with different heating rates compared to the equilibrium magnetization curve. The equilibrium magnetization curve was obtained after connection of magnetization values at different temperatures with a temperature interval of 20–30 K, while the magnetization values were measured in the equilibrium state (*i.e.* after waiting for 5000 s). The equilibrium magnetization curve was similar as the magnetization curve M_s in Figure 1B.

In Figure 2, it can be seen that the temperature-dependent magnetization M-T curves taken at different heating rates deviate from the equilibrium magnetization curve. When the heating rate was low (3 K/min), the deviation from the equilibrium curve is small, especially no significant deviation is found at lower temperatures (< 140 K). When the heating rate was 10 K/min, the M-T curve was well above the equilibrium M-T curve in the temperature range of 10–138 K, and was significantly below the equilibrium M-T curve from 150 K to 295 K. The deviation indicates the possible presence of magnetic relaxation. In this work, we have studied magnetic relaxation in the temperature range of 10 to 300 K. Only small magnetic relaxation effect was found when temperature was below the compensation temperature (10–138 K). Therefore, the study was concentrated on the temperature range of 138–300 K.

As shown in Figure 2, a large deviation between the equilibrium magnetization curve and the M-T curves was

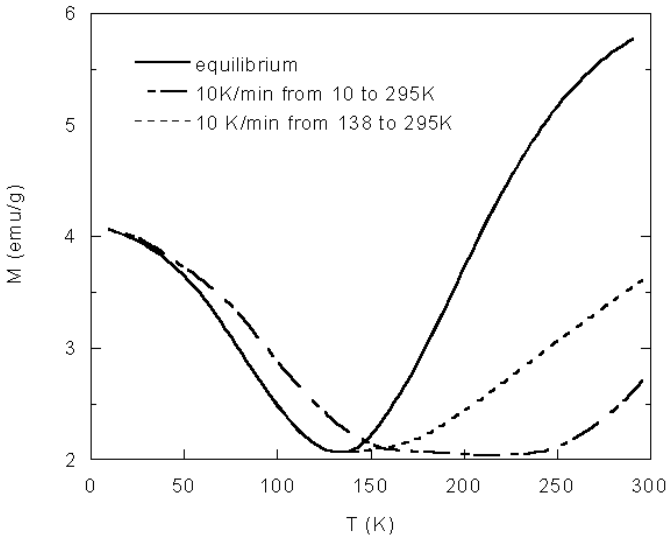

Fig. 2. Temperature-dependent magnetization curves (M-T) of $MoFe_2O_4$ with different heating rates compared to the equilibrium magnetization curve.

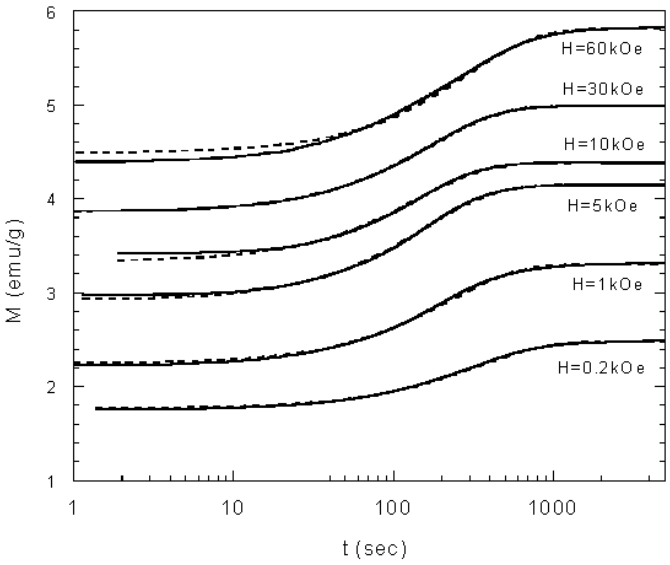

Fig. 3. M-t curves of $MoFe_2O_4$ taken at 295 K under different constant fields (0.2–60 kOe) after heating from 138 K with a heating rate of 10 K/min. Solid lines are measured magnetization curves, while dashed lines are fitting curves from equation (1).

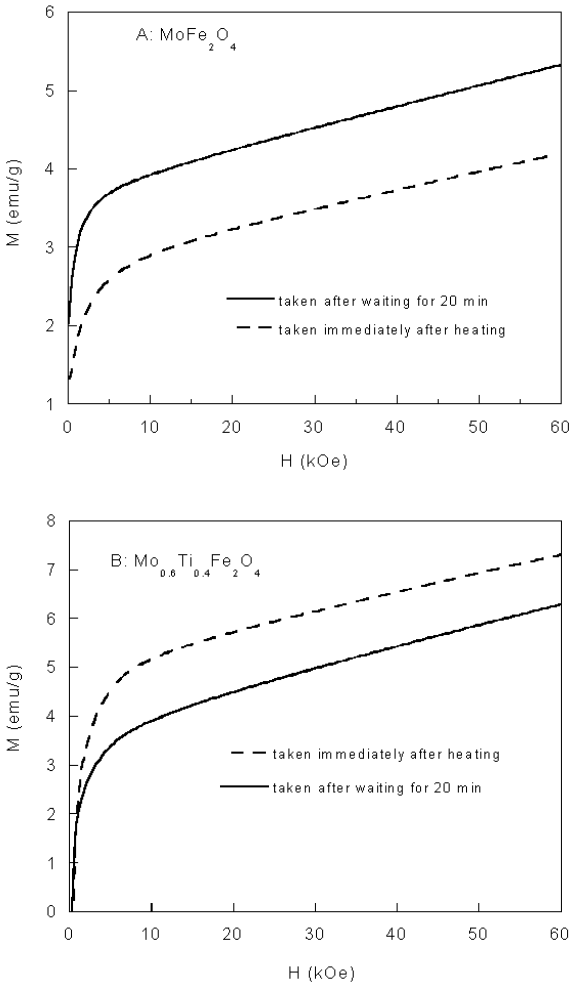

Fig. 4. A) magnetization curves of $MoFe_2O_4$ at 295 K taken immediately after heating from 138 K with a heating rate of 10 K/min and taken after waiting for 20 minutes after heating from 138 K with a heating rate of 10 K/min; (B) magnetization curves of $(Mo_{0.6}Ti_{0.4})Fe_2O_4$ at 295 K taken immediately after heating from 175 K with a heating rate of 10 K/min and taken after waiting for 20 minutes after heating from 175 K with a heating rate of 10 K/min.

also present in the temperature range between 138 and 295 K. Large magnetization relaxation was found in the temperature range of 138–295 K. A detailed study on magnetic relaxation was conducted for the temperature range. Figure 3 shows M-t curves taken at 295 K after heating from 138 K with a heating rate of 10 K/min, while a constant magnetic field (between 0.2 to 60 kOe) was applied. It can be seen that magnetization relaxation is not strongly dependent on magnetic field from 0.2 kOe to 60 kOe. From hysteresis loops (Fig. 1A), no change in domain structure is expected, when magnetic field is above 0.5 kOe. As it can be seen, the major change in magnetization occurred in the time range of 100 to 1000 s. All the M-t curves taken at 0.2–60 kOe could be well fitted with the function [12]:

$$M = M_0 + A\exp(-t/\tau) \quad (1)$$

where M_0 is the magnetization after equilibrium, A is a coefficient, t is time and τ is the relaxation time. After fitting with equation (1), τ was around 200 s for all the M-t curves. This result supports that the magnetization relaxation is attributed to the transition between different states (compensated and uncompensated) and is not due to change in domain structure.

Figure 4A shows the magnetization curves (measured from the initial magnetic field of 60 kOe to zero field) of $MoFe_2O_4$ taken immediately after heating from 138 K and taken after a waiting for 20 min after heating from

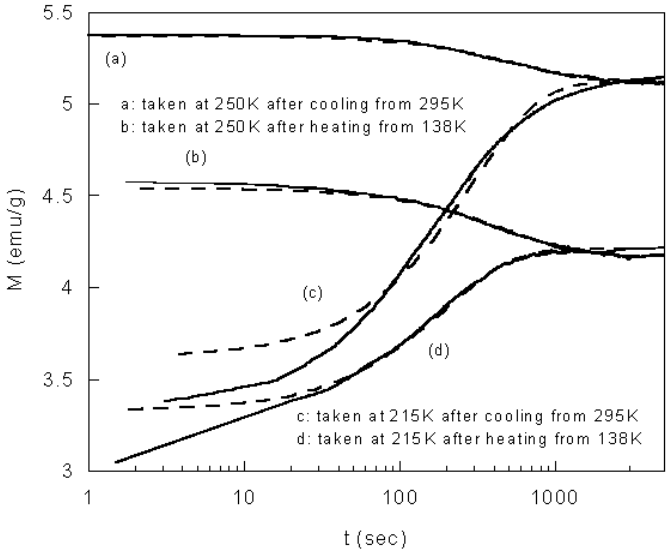

Fig. 5. M-t curves of $MoFe_2O_4$ taken at 215 K and 250 K after heating from 138 K and cooling from 295 K, respectively, with a heating/cooling rate of 10 K/min. Solid lines are measured magnetization curves, while dashed lines are fitting curves from equation (1).

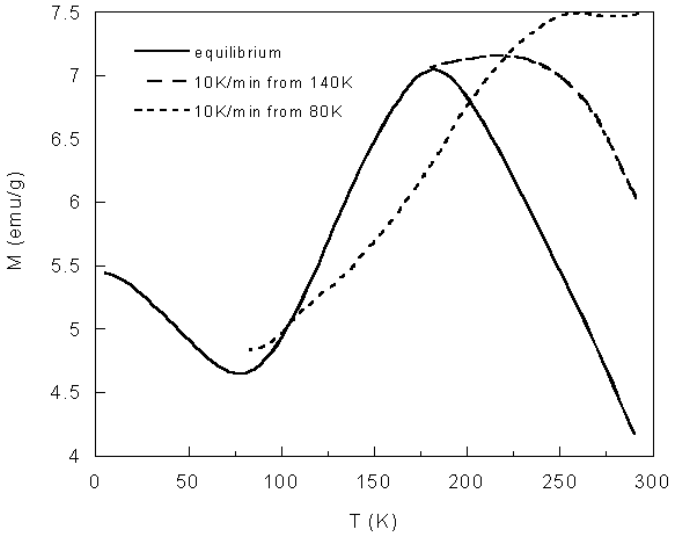

Fig. 6. Temperature-dependent magnetization curves (M-T) of $(Mo_{0.6}Ti_{0.4})Fe_2O_4$ with different heating rates compared to the equilibrium magnetization curve.

138 K. It can be seen that the major change between the two curves is the magnetization at low fields, while the slope of dM/dH roughly remains unchanged. This result confirms that the magnetic relaxation is mainly caused by the uncompensated magnetic moment.

From the above study, it is possible that there is a transition in magnetic state existing in the temperature range of 138–295 K. The mechanism of the possible transition in state has to be investigated. Our study indicated that the magnetic relaxation is mainly caused by the increase in uncompensated magnetic moment, *i.e.* a possible transition from compensation to non-compensation.

Figure 5 shows M-t curves taken at 215 K and 250 K after heating from 138 K and cooling from 295 K, respectively. Magnetic relaxation was evident in the both curves after cooling and heating, but with different signs. When fitting with equation (1), the curves after heating from 138 K had a τ value of 200–250 s, while a much larger τ value of 600–700 s was found for the curves after cooling from 295 K. After waiting for 5000 s, there was no noticeable change in magnetization. The sample reached the equilibrium state after 5000 s for waiting. It is to note, that the equilibrium magnetization (after waiting for 5000 s) after cooling from 295 K was lower than that after heating from 138 K. This result indicates that the magnetic moment is dependent on the origin spin-state (compensated or uncompensated).

3.2 $(Mo_{0.6}Ti_{0.4})Fe_2O_4$

Unusual magnetic properties with compensation temperature have been reported in Ti substituted $MoFe_2O_4$ [8]. Our previous study on $(Mo_{0.6}Ti_{0.4})Fe_2O_4$ indicated the presence of homogeneity and cluster-glass behavior [8]. A magnetic ordering temperature was estimated to be ∼265 K from magnetic and Mössbauer examinations. However, weak magnetization was evident at room temperature [8]. These results suggested magnetic Mo-rich clusters embedded in antiferromagnetic Ti-rich matrix with a Néel temperature of ∼265 K.

In this work, we have studied magnetic relaxation in $(Mo_{0.6}Ti_{0.4})Fe_2O_4$. Figure 6 shows magnetization M-T curves of equilibrium and taken during heating with a heating rate of 10 K/min from 80 K and 175 K respectively. The magnetic behavior was more complicated than that of $MoFe_2O_4$ as shown in Figure 2. A compensation was observed at ∼100 K. There was a maximum of magnetization at 175 K. No significant magnetic relaxation was observed in the temperature range of 4–100 K. Therefore, our study was focused on the temperature range of 100–300 K (heating or cooling from 100, 175 and 300 K, respectively).

When the $(Mo_{0.6}Ti_{0.4})Fe_2O_4$ sample was heated from 100 K to a temperature of 120–175 K, magnetic moment increased with time under a constant field. All the M-t curves could be well fitted with equation (1). The relaxation time τ_1 (heating from 100 K) was in the range of 90–110 s.

If the sample was heated from 175 K, a negative magnetic relaxation (decrease of moment with time) was observed in the temperature range of 200–295 K with τ_2 = 200–300 s (corresponding to heating from 175 K). Figure 7A shows M-t curves taken at 235 after heating from 100 and 175 K respectively. When the sample was heated from 175 K, M-t curves could be well fitted with equation (1). Relaxation time was estimated to be around 250 s.

When the sample was heated from 100 K to 235 K, M-t curves changed significantly compared to those after heating from 175 K. The shape of the M-t curves could not be simply fitted with equation (1). Magnetization went

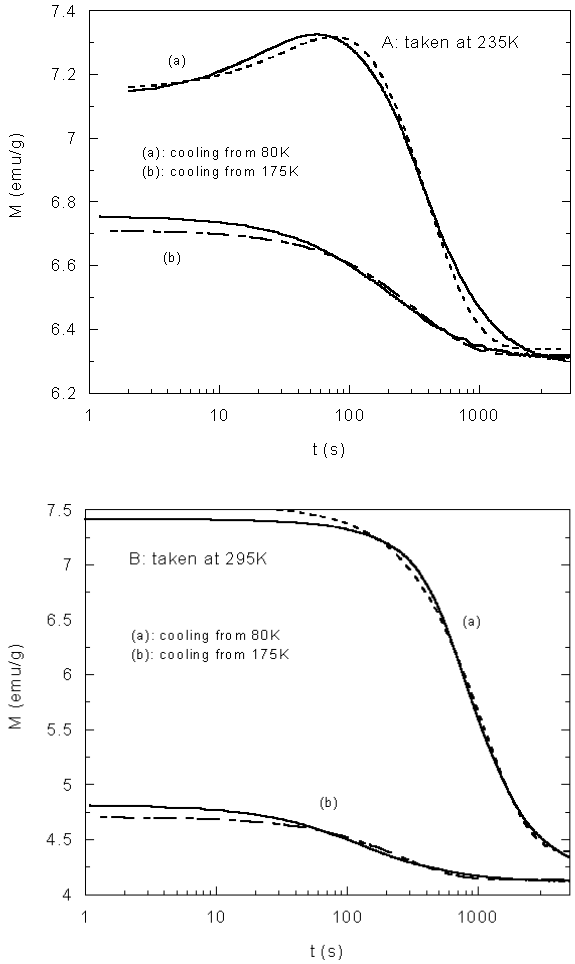

Fig. 7. M-t curves of $(Mo_{0.6}Ti_{0.4})Fe_2O_4$ taken at 235 K (A) and at 295 K (B) after heating from 100 K and 175 K respectively. Solid lines are measured magnetization curves, while the dashed line for the curve taken at 235 K after heating from 100 K is fitted with Eg. 2 and the rest dashed lines are fitting curves from equation (1).

up initially and decreased afterward. The magnetization curve could be well considered as a combination of two relaxation processes, as described below:

$$M = M_1 + M_2 \exp(-t/\tau_2) + M_3 \exp(-(t/\tau_2 + t/\tau_1)) \quad (2)$$

where $\tau_2 = 250$ s and $\tau_1 = 90$ s are relaxation times for the transitions from 175 K to 295 K states and from 100 K to 175 K, respectively. The M-t curve taken at 250 K after heating from 100 K could be well fitted with equation (2), as shown by the dashed line in Figure 7A.

Figure 7B shows M-t curves taken at 295 K after heating from 100 K and 175 K respectively. When the sample was heated from 175 K to 295 K, the M-t curve could be well fitted with equation (1) with a relaxation time of ∼250 s. When the sample was heated from 100 K, a much large relaxation was observed. The M-t curve could not be well fitted with equation (2). When fitted with equation (1), the relaxation time went to a much high level – 1200 s. The initial part of the M-t curve (at short time <200 s) could not be well fitted with equation (1). It can be seen that magnetization had not reached the equilibrium even after 5000 s. This result indicates that spins are in a more complex situation, and the magnetic relaxation is strongly dependent on the initial spin state. A modified equation of $A + B\exp(-(t/\tau_0)^\alpha)$ with $\alpha \approx 0.7$ could fit the M-t curve better. This result indicates that strong interactions between spins in different states may exist, as proposed in spin glass and other systems [9].

As shown in Figure 5, magnetic relaxation could be observed in the both ways after heating from 138 K and after cooling from 295 K for the Mo-ferrite sample. However, for the Ti-substituted $(Mo_{0.6}Ti_{0.4})Fe_2O_4$ sample, no significant magnetic relaxation could be detected after a cooling process.

Figure 4B shows the magnetization curves (measured from the initial magnetic field 60 kOe to zero field) of $(Mo_{0.6}Ti_{0.4})Fe_2O_4$ taken immediately after heating from 175 K and taken after a waiting for 20 min after heating from 175 K. Again, this result indicates that the magnetic relaxation is mainly caused by the uncompensated magnetic moment.

4 Conclusion

$MoFe_2O_4$ showed a compensation temperature of 138 K. Slow magnetic relaxation was observed from the compensated state at the compensation temperature to an uncompensated state (with a temperature higher than the compensation temperature). The magnetic relaxation was nearly independent on magnetic field. Hysteresis loops taken at different times indicated clearly that the magnetic relaxation was due to uncompensated magnetic moment. Magnetic relaxation was also dependent on the initial state (compensated state, uncompensated state below or above the compensation temperature). It has been found that the values of equilibrium magnetization were different after heating or cooling process. All the time-dependent magnetization curves could be well fitted with equation (1). The relaxation time τ was 200–300 s after heating from 138 K (from compensated to uncompensated). When the sample was cooled down from 295 K, τ increased in the range of 600–700 s (from uncompensated to compensated).

For $Mo_{0.6}Ti_{0.4}Fe_2O_4$, the magnetic susceptibility had a complicated process (consisting of a compensation at 100 K and a maximum of magnetization at 175 K). Slow magnetic relaxations were observed. When time-dependent magnetization curves were taken at a temperature in the range of 120–175 K after heating from 100 K, the relaxation time τ was 90–110 s. In the temperature range of 175–295 K, τ was measured to be 200–300 s after heating from 175 K. When the sample was heated from 100 K to 235 K, the M-t curve could be considered as two magnetic processes. However, at 295 K, magnetic relaxation exhibited a complex behavior after heating from 100 K. No significant magnetic relaxation was observed after a cooling process.

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